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AFRPL-TR- 67 - 60

(Unclassified Title)

KINETICS OF DECOMPOSITION
OF SOLID OXIDIZERS

ANNUAL TECHNICAL SUMMARY REPORT AFRPL - TR - 67 - 60
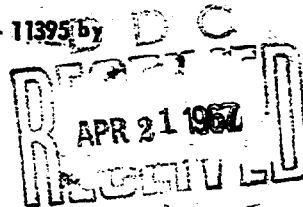
(1 January 1966 to 31 DECEMBER 1966)

15 JANUARY 1967

AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
EDWARDS AIR FORCE BASE, CALIFORNIA

APR 21 1967

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AFRPL-TR-6?-?0

January 15, 1967

This document consists of 89
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ANNUAL TECHNICAL SUMMARY REPORT

(1 January - 31 December 1966)

KINETICS OF DECOMPOSITION
OF SOLID OXIDIZERS   (U)

January 15, 1967

Dow Report NF-4Q-66

AIR FORCE SYSTEMS COMMAND
RESEARCH AND TECHNOLOGY DIVISION
ROCKET PROPULSION LABORATORY
EDWARDS, CALIFORNIA
CONTRACT NR. AF 04(611)-11395

SCIENTIFIC PROJECTS LABORATORY
THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN

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FOREWORD   PAGES NOT FILMED ARE BLANK

This report was prepared by The Dow Chemical Company, Midland, Michigan, on Air Force Contract Nr. AF 04(611)-11395, BPSN 623148, Project Number 3148, "Kinetics of Decomposition of Solid Oxidizers." This work was sponsored and administered by Air Force Rocket Propulsion Laboratory, Research and Technology Division, Edwards, California, Air Force Systems Command, United States Air Force, with Dr. William J. Leahy as project officer.

The report represents the work performed on this contract for the period of 1 January - 31 December 1966, and is being submitted as the Annual Technical Summary Report as part of the contract commitment.

Management direction at Dow is under Dr. R. P. Ruh, Laboratory Director of the Scientific Projects Laboratory, and supervised by Dr. D. A. Rausch, Division Leader. Dr. J. P. Flynn and Mr. T. E. Dergazarian are the principal investigators. Dr. R. G. Pearson, Northwestern University, is a consultant to the project.

The principal investigators were assisted in the laboratory work by Mr. G. D. Sellers.

This report has been reviewed and is approved.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

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SECTION I

(U) ABSTRACT

(U) The purpose of this research was to study the thermal decomposition of the solid oxidizers, INFO-635P, poly FA-BDE, and BTU. The objective was to obtain knowledge of their decomposition mechanisms and their relationship to the high sensitivity of these materials.

(U) The degradation of INFO-635P and poly FA-BDE was investigated chiefly by performing decompositions in the temperature range, 160°-180°C., under conditions of continuous vacuum, and low and high pressure of product gases. In addition, the technique of mass spectroscopic thermal analysis (MTA), complemented by high-resolution mass spectroscopy, was used to study the decomposition under high vacuum where secondary reactions were minimized.

(C) Examination and interpretation of the experimental data have shown that INFO-635P may decompose, after nucleation, by one or more of several paths simultaneously. This multiplicity of reaction mechanisms is mainly a result of the sublimation of INFO-635P, which appears to obey a first order rate law. This physical process is presumed to occur after a series of reactions in the solid phase involving proton transfer and desorption from the solid of the resulting free amine and perchloric acid into the gaseous state.

(C) The products from the gas phase reaction are N_2F_4, N_2F_2, HNF_2, HF as SiF_4, CO_2, N_2O and N_2. The solid from such a reaction is mainly unreacted INFO-635P. The products from the more rapid solid phase reaction are CO_2, N_2O, NO, N_2, HF as SiF_4 and some N_2F_2. The residue is an intractable combination of materials, one of which was identified as ammonium perchlorate. There are at least two more materials, one of which may be a halogenated organic carbonyl perchlorate, and the other a highly halogenated polymer.

(C) Desensitization of INFO-635P may be possible; at least the proton transfer step may be successfully prevented either by reversing the proton transfer step with the addition of anhydrous perchloric acid or by removing the proton and making the quarternary methyl ammonium salt, $(CH_3)_3N^+ClO_4^-$.

(C) The experimental results on poly FA-BDE showed that the early gaseous products of decomposition are N_2F_4, N_2F_2, N_2, NO, CO, COF_2, HNF_2, HF and NF_3, leaving a residue which becomes progressively less sensitive as decomposition proceeds. At the end of the first phase of the decomposition, the "final" product gas mixture consists of N_2, HF, CO_2, NF_3, CF_4, and N_2O with

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an insensitive and insoluble residue believed to be a highly crosslinked polymer containing many carbon-fluorine and carbon-nitrogen bonds. Experimental substantiation is given for the first step which is cleavage of the carbon-nitrogen bond to form difluoroamino free radicals. Mechanisms are proposed for the early degradative steps which explain the formation of the observed products. The reason for the exothermicity and high sensitivity of poly FA-BDE is given as due to the formation of HF from fluorine and RH and possibly to the rapid decomposition of an unstable intermediate, perfluorourea, $[O=C(NF_2)_2]$, which would decompose to the thermodynamically favored COF_2, N_2 and F_2. The experimental results give little hope for the desensitization of this material.

(C) Experimental work on BTU was limited to purification of small quantities for several preliminary thermal decomposition experiments. Mass spectroscopic methods proved to be of no value on this compound because of its tendency to sublime. Slow thermal decomposition studies showed that BTU decomposes in the vapor phase only to yield TRIS-I $[(NF_2)_3CNCO]$ as an early product together with N_2, HF, CF_4 and NF_3.

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SECTION II

(U) INTRODUCTION

(U) The purpose of this research has been to obtain new, basic information on the kinetics and mechanisms of thermal decomposition of the three solid NF-containing oxidizers, INFO-635P, BTU, and poly FA-BDE. These compounds are sensitive, hence hazardous materials, and, because of this their utility has been severely limited. The ultimate objective of this investigation was to achieve an understanding of this high sensitivity in order to better assess the probability of decreasing the sensitivity to an acceptable level.

(U) To accomplish these objectives, two experimental approaches have been utilized, viz., slow thermal decompositions in a monel system and mass spectrometric techniques which permitted decomposition of small samples within 2-3 mm. of the ionizing electron beam. In the slow thermal decomposition method, the decomposition gases and residues were sampled and analyzed as a function of time and temperature from which the necessary kinetic data were derived. Mass spectrometric techniques, under very high vacuum, minimize secondary reactions involving the decomposition gases and thus have the potential for detecting the first step in the decomposition process. Throughout this study, the emphasis has been on the detection of the first step and the determination of the initial stages of the thermal decompositions.

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SECTION III

(U) BACKGROUND INFORMATION ON THE OXIDIZERS

A. INFO-635P, $(NF_2)_3C-O-CH_2CH_2NH_3^+$ ClO_4^- (C)

(C) INFO-635P is a white crystalline solid first made at Minnesota Mining and Manufacturing Company (3M) by adding ethanolamine perchlorate to perfluoroguanidine, followed by fluorination of the adduct. The heat of formation of this compound has been evaluated as 113.6 ± 10 k.cal./mole (1).

(U) INFO-635P is a shock and spark sensitive material. Minnesota Mining has reported a value of 5.5 kg.-cm. for the impact sensitivity of the purified material and Aerojet found it to be 3 cm. with a 2 kg. weight. Allegany Ballistics Laboratory compared INFO-635P with nitroglycerin on its impact tester and obtained 8.6 cm. for the former and 11-13 cm. for the latter. The Naval Ordnance Test Station conducted electrostatic sensitivity tests and reported a value of 0.002 joules as compared with 12.5 joules for HMX.

(U) The density of the pure solid is reported by 3M to be 1.86 ± 0.06 g./cc. The melting point depends largely upon purity and is reported as low as 195°C. and as high as 226°C. (2). In any case, the solid melts with vigorous decomposition leaving a residue.

(U) Taliani gas evolution tests (2) on pure samples indicated no decomposition at 60°-70°C. for ten days. At 80°-90°C. decomposition began slowly after four days. The impure salt is less thermally stable, e.g., a sample of 90% purity was not stable for an extended period at 67°C.

(U). Examination by differential thermal analysis indicated no apparent decomposition until the temperature reached 150°C. Rapid decomposition occurred at 182°C. On a hot stage, bubbling was observed at about 110°C. and continued until a residue remained at 210°C. (3). The pure salt was found to be incompatible with compounds containing hydroxyl or amino groups and with nitrate esters. It appeared compatible with hydrocarbons such as heptane and cyclohexane and acids such as acetic.

(C) The slow thermal decomposition was studied in aqueous base and acid (4). The study showed that the free amine of INFO-635P decomposed rapidly at room temperature by forming a three-membered intermediate involving the amino group, resulting ultimately in ethylenimine. There appeared to be little doubt that NF_2 radicals were produced, and it was postulated that their formation was the initial step, followed by cyclization of the remaining two NF_2 groups. It was suggested that the presence of even small amounts of the free amine in the perchlorate salt might be the source of a detonation.

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(U) Preliminary studies on the decomposition of the solid have been made in the temperature range 140°-215°C. at U. S. NOTS (5,6). These early results indicated an effect of product gases on the decomposition and a dependency of reaction rate on total pressure.

B. BIS [TRIS(DIFLUOROAMINO)METHYL]UREA, "BTU", [(NF$_2$)$_3$C-NH]$_2$C=O (C)

(U) Information on the preparation and properties of BTU is detailed in reports of American Cyanamid Company (7,8). The heat of formation is reported by them to be -82.7 ± 2.2 kcal./mole, while, more recently, The Dow Chemical Company reported -73.7 ± 4 kcal./mole (9).

(U) BTU is a white crystalline solid and when sublimed or properly recrystallized forms needle-like crystals having cross-sections of a few microns and lengths up to several millimeters. The compound is particularly friction-sensitive, which constitutes the greatest hazard. The impact sensitivity has been reported as high as 38 kg.-cm. on early preparations, and more recently (10) as 28-30 kg.-cm. on pure sublimed crystals.

(U) Experimental work by American Cyanamid has shown that when the compound is purified by sublimation it has substantially better thermal stability than when the purification is by re-crystallization from solvents or solvent mixtures. The difference in stability appears to be due to a tendency of the crystals to occlude solvent. In this regard, best results have been obtained from a chloroform-isooctane system which yielded 90-95% inclusion-free crystals. In any event, for maximum stability it was neces-sary that the BTU be kept scrupulously free of water. This lat-ter fact was clearly shown in rate studies on the decomposition of BTU in diglyme solution in which the presence of small amounts of water greatly increased the decomposition rate. In dry diglyme, the decomposition was first order in BTU with k = 9.3 x 10^{-5} sec.$^{-1}$ at 110.5°C.

(U) Differential thermal analysis of BTU in sealed ampoules did not indicate an exothermic reaction until about 130°C. The rate of decomposition increased at 158°C., reached a peak at about 180°C., and then dropped back to the base line at 190°C. A second exothermic peak began immediately, peaked near 195°C., and then fell slowly back to the base line.

(U) Some rate studies on the decomposition of the solid were made by American Cyanamid Company (8) at 119.5°C. Although the data had considerable scatter, they did show that the reaction followed a first order law reasonably well with k = 1.8 x 10^{-5} sec.$^{-1}$, approximately. Preliminary data on solid BTU were also obtained in work at NOTS (5). Decompositions were carried out between 130°-150°C. under a pressure of 200 mm. of nitrogen. An Arrhenius plot of the data was reasonably linear and gave an apparent activation energy of 24 kcal./mole and a pre-exponential factor of 10^9.

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C.   POLY FA-BDE   (U)

(C)   Poly FA-BDE was first prepared by Esso Research and Engineering Company (11) as a white solid by the polymerization of FA-BDE (fluorinated PFG adduct of butendiol epoxide) using SbCl5 as catalyst. Although the usual preparatory route produces a fine powder, a process has now been developed to make the polymer in the form of beads several microns in diameter (12).

(C)   The spark sensitivity of poly FA-BDE is serious, requiring less than 0.0016 joule to explode test samples. The impact sensitivity is intermediate for this type of compound, viz., 22 k.-cm. for both powder and bead forms. Esso made an extensive study of the physical and chemical properties of this material and most of these data are summarized in one report (13). The heat of formation was estimated to be about -112.7 kcal. per polymer unit. The polymer melts, apparently with decomposition, at $202°-204°C.$, and exhibits an autoignition at about 253°C. Its thermal stability appears to be superior to INFO-635P. Vacuum stability tests showed no measurable gas evolution until 90°C., at which temperature 2.77 cc. of gas per gram of polymer were evolved after 100 hours. The evolved gas consisted of NO, CO_2, N_2F_4, and HF.

(U)   Thermogravimetric analysis of the polymer showed no weight loss up to about 155°C., at which point the sample began losing weight and continued until decomposition was complete. Differential thermal analysis indicated that exothermic decomposition began about 160°C. and peaked at 218°C., the former figure corresponding well with the beginning of weight loss at 155°C.

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SECTION IV

(U) DISCUSSION OF RESULTS

A. INFO-635P (U)

1. Thermal Decomposition Background (U)

(U) Considerable work has been reported in the literature (14-17) on the kinetics of solid state decompositions. The thermal breakdown of a crystalline structure is neither physically nor chemically a simple process, and usually gives a wide variety of end-products which may be solid, liquid or gaseous. The major effort reported in the literature has been the examination of the physical breakdown of the crystalline lattice during thermal decomposition.

(U) With many reactions in the solid state, lattice imperfections or crystal dislocations play an important role, because the rate controlling step frequently is the diffusion of a reactant or a product through the reaction layer. This diffusion is possible only by virtue of the lattice defects, which implies that the effect of the physical factors such as particle size distribution and particle shape should be considered (18,19). For example, finely divided solids react more rapidly with gases than do the coarser solids. The thermal decomposition of a single solid substance accompanied by a change of phase is complex due to the diffusion processes, interface reactions and the creation of a new phase or nuclei from which the product phase spreads or grows. Therefore, in solid state reactions, the concepts of concentration and order of reaction generally have no significance.

(U) The definition of a rate constant $\underline{k}$ and an activation energy $\underline{E}$ for a solid state reaction, in analogy with a reaction taking place in the gas phase, gives rise to several difficulties. In a gaseous reaction the concentration is expressed as a continuous real valued function of time, and the mechanism of the reaction is expressed by a system of differential equations, the solution of which gives the concentration of various reactant species and their rate constant $\underline{k}$. The activation energy $\underline{E}$ is derived from the dependence on temperature of $\underline{k}$ according to Arrhenius' law. If the same conditions are assumed for a solid state reaction, $\underline{k}$ must be independent of time and have the factor of reciprocal seconds in its dimensional formula for a first order reaction and increases with temperature according to an exponential law from which an activation energy could be derived. This latter condition will not be fulfilled for solid state reactions, since the assumption for gas reactions of an equilibrium between activated and non-activated molecules according to the Boltzman distribution is not valid. Therefore, a rate constant cannot be defined for a solid state reaction in the same way as for reactions in gases.

(U) The reaction rate of a solid state reaction is usually characterized by the rate at which the reaction zone increases, and is defined as the change with time of the thickness of the

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layer of product formed (20). This depends essentially on two types of processes: (1) the physical process of diffusion of the reactants through the reaction layers, and (2) the chemical reactions and the chemical processes which are produced at the reaction interface. Usually one of the two processes is much slower (19) and constitutes the rate determining step. The kinetic expression of the reaction will then be defined by the nature of this determining step. If the chemical process prevails, then, for solid state reaction kinetics, the rate constant and activation energy can be defined only when a suitable hypothesis for the mechanism of the given reaction is available.

(U) Little progress has been made in transforming the overall chemical process of a solid state decomposition into a series of kinetically simple chemical changes as has been done successfully with gaseous and solution reactions. One of the principal goals of the present study is to determine the chemical reactions and the chemical processes that are produced at the reaction interface. This may be achieved by an analytical and kinetic study of the solid, liquid or gaseous products formed during the course of the decomposition. The first stage of an experimental study of a thermal decomposition is usually the determination of a curve representing the plot of the fraction decomposed (α) or of pressure as a function of time (t). The typical curves for α vs. t are generally sigmoid, indicating an autocatalytic reaction. The curve may be divided into three segments, an induction period, an acceleratory period, and a decay period. The curve may be symmetrical or asymmetrical. Each period may either be of short duration or very pronounced.

(U) The exothermic solid reactions of the type $A(s) \rightarrow B(s) + C(g)$ can be classified according to the shape of the pressure-time curves (p vs. t) obtained during thermal decomposition (20). There are three main types. In the first type, a rapid rate of reaction occurs at the beginning of decomposition and is typical of solids wherein the nuclei of the new phase are rapidly formed, resulting in an almost instantaneous coverage of the surface with a film of solid product. Lead and silver azides are good examples of this behavior. In the second type, there is an apparent induction period due to a slow rate of production of nuclei, as exemplified by barium azide. The third category is characterized by a small initial gas evolution, which is most rapid at the beginning of the heating, which is then followed by an acceleration of the reaction as in the second type of curve. Mercury fulminate, potassium azide, and lithium aluminum hydride are good examples of the third type.

(U) INFO-635P is unusual because its decomposition appears to have characteristics common to both inorganic and organic solids. The available information for inorganic solids suggests that there is no dramatic change in the physical properties of solids at temperatures very close to the melting point. If slow decomposition

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occurs below the melting point, then crystal break-up is an important process. If the break-up takes place during a fast reaction, and there is strong evidence for this (14), then the rate of decomposition can be considerably increased by exposing a large surface area of the material.

(U)   For organic solids, the decomposition mechanism is different from an ionic inorganic solid. The majority of organic solids are stable below the melting point and pass into the liquid state without decomposition. There are, however, numerous cases where melting occurs with decomposition, such as organic azide and diazo-compounds. Many of these decompositions form a product which lowers the melting point of the initial substance, and, generally, it can be shown that a sigmoid-shaped, pressure-time curve would result if partial liquefaction occurred during the decomposition. The formation of a liquid phase has a considerable influence on the rate of decomposition (14).

(U)   The hot stage microscopy work on INFO-635P shows that partial liquefaction does occur when there is a constant heating rate. Also, examination of the residues from the monel reaction decompositions in the presence of the product gases indicates that liquefaction has occurred, since the residue, a viscous liquid plus a solid, has tended to flow and collect at a low point in the reactor.

(U)   In the present work, the effort has been directed toward making the chemical process rather than the nucleation the slow step in decomposition. This has been accomplished by increasing both sample size and surface area and narrowing the particle size distribution. However, the sublimation and subsequent decomposition in the vapor phase has completely masked any slow chemical process in the solid.

(U)   The specific order in which each type of experiment was run is not the order in which the following results are discussed, but rather in a sequence determined by the total results. Total pressure decomposition in the monel system were run first. The results from these decompositions lead to experiments run under partial and continuous vacuum in the monel system and eventually to a glass system.

(U)   A monel metal reactor and vacuum manifold were selected because the metal surface, once passivated with fluorine gas, would be inert toward any further surface reaction.

2. DTA and TGA   (U)

(U)   The compound INFO-635P was examined by both DTA and TGA methods with the objective of ascertaining the best temperature

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range to make decomposition studies. The first set of data was obtained on freshly recrystallized material. The initial heating rate for the DTA and TGA experiments was 10°C./minute and at 150°C. was changed to 2°C./minute. For the TGA, a 20 mg. sample was heated in vacuum. A weight loss of 3% occurred abruptly at 33°C. The sample then volatilized at a moderate rate until a weight loss of 10% was reached at 136°C. The rate of volatilization began to increase rapidly at about 148°C. so that at 185°C. the loss was 97.5%. In the DTA about 10 mg. was mixed with calcined Al_2O_3 which was used as reference. An endothermic drift began at approximately 34°C., correlating with the volatilization observed in the TGA. A weak, but sharp, endotherm was recorded at 159°C. At about 175°C. a strong exotherm began, reaching a maximum at 206°C. A second DTA, made the following day, duplicated the first result except that the weak endotherm appeared at 162°C.

3. Vacuum Decomposition (U)

a. Partial and Continuous Vacuum Decomposition in a Monel System (U)

(U) Analysis of the data from three decompositions at 170°C., in which the pressure of the product gases over the solid were not allowed to exceed a specific limit. Figure 1 and 2 reveal that gas-solid and gas-gas interactions are significant.

(C) The product gases from one partial vacuum run at 170°C. were chromatographed. The results, shown in Figure 3, indicate the N_2F_4 has reached an apparent steady state which is compatible with data obtained on other high energy NF compounds, and suggests the C-N bond cleavage is important, though it is not yet obvious whether the N_2F_4 is a result of a solid or gas phase reaction.

(C) The experimental results from a series of decompositions of INFO-635P that were run under continuous vacuum are given in Figure 4 and Table I. The percent weight loss curve appears to be very regular and to stabilize at about 85%. The mass spectral data of product gases show a general trend in the total concentration of product gases as a function of time. There is no nitrogen gas because the particular technique employed in maintaining a continuous vacuum does not allow the identification or determination of non-condensable gases. Some of the minor gaseous products also found are C_2H_2, C_2H_4, CH_3NH_2, CNCl, $C_2H_2F_2$, CF_4, and SiF_4. A liquid was also collected with these gases from the vacuum decompositions; however, once collected in the Kel-F trap the liquid could not be vacuum-transferred out of the trap for analysis.

b. Mass Spectral Study of the Thermal Decomposition (U)

(U) A portable cycloidal mass spectrometer, on loan from the Chemical Physics Laboratory of The Dow Chemical Company, was

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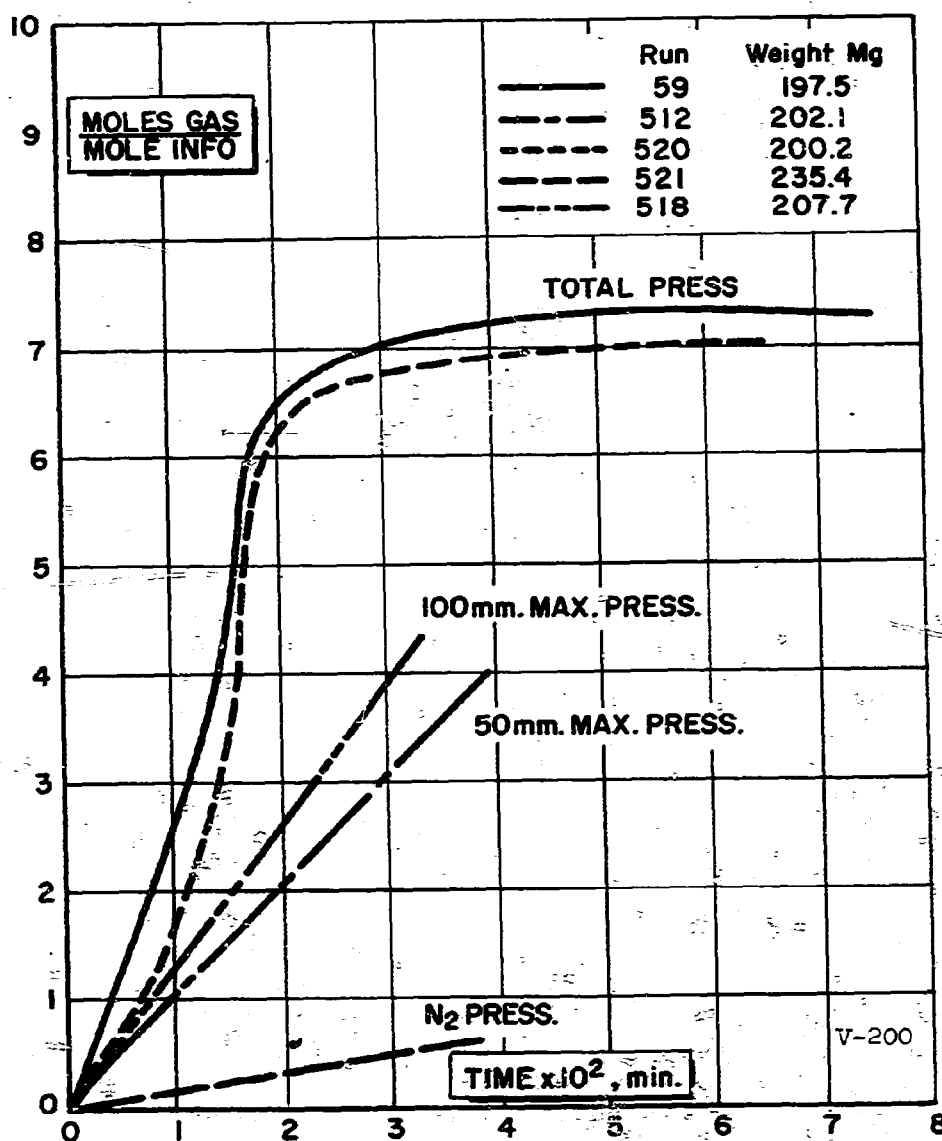
(U) Fig. 1 – Pressure-Time Curves for INFO-635P
Decomposition at 170°C.
In Monel Reactor.

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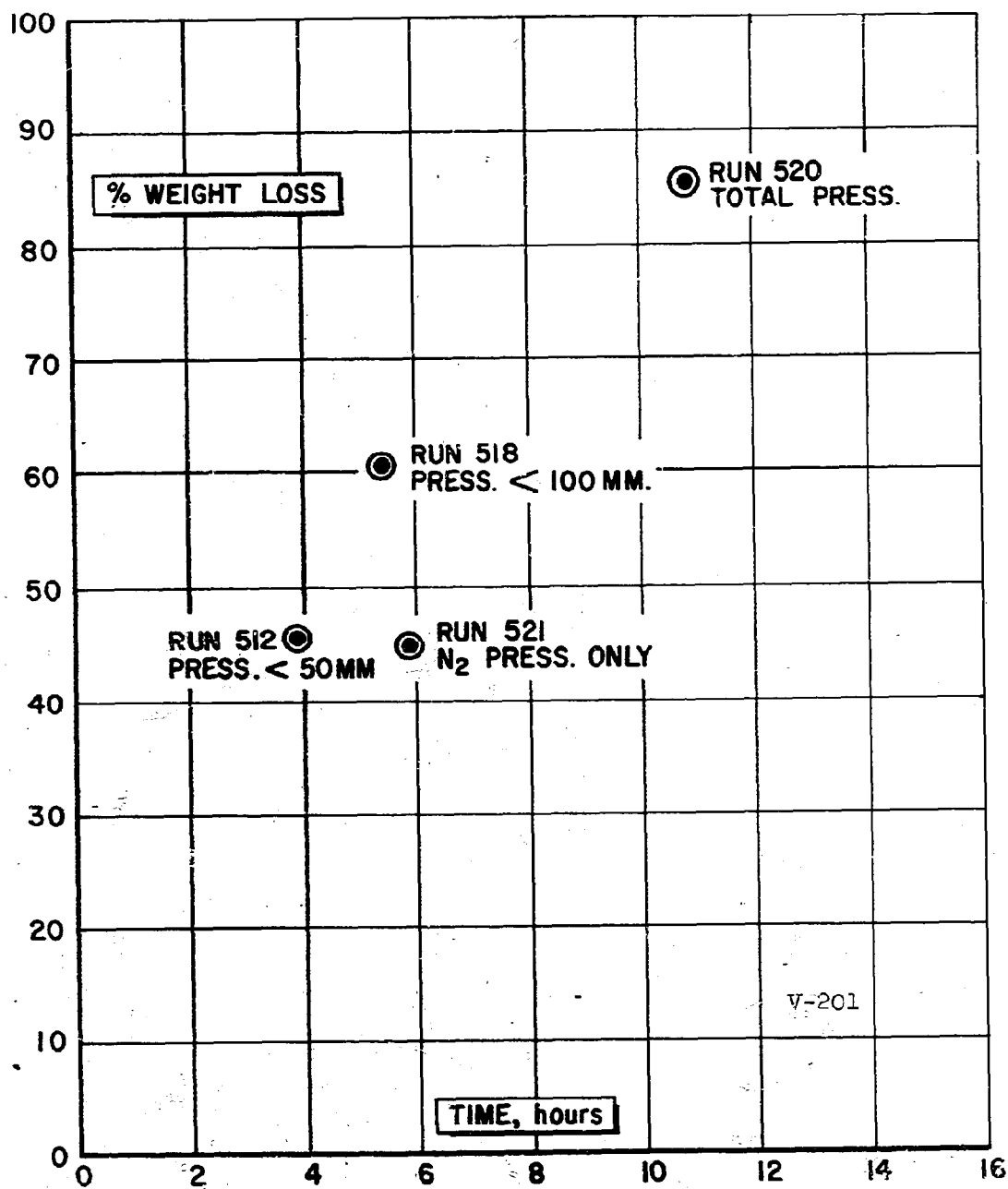
(U)   Fig. 2 – Percent Weight Loss of
Solid INFO-635P at 170°C.
In Monel Reactor.

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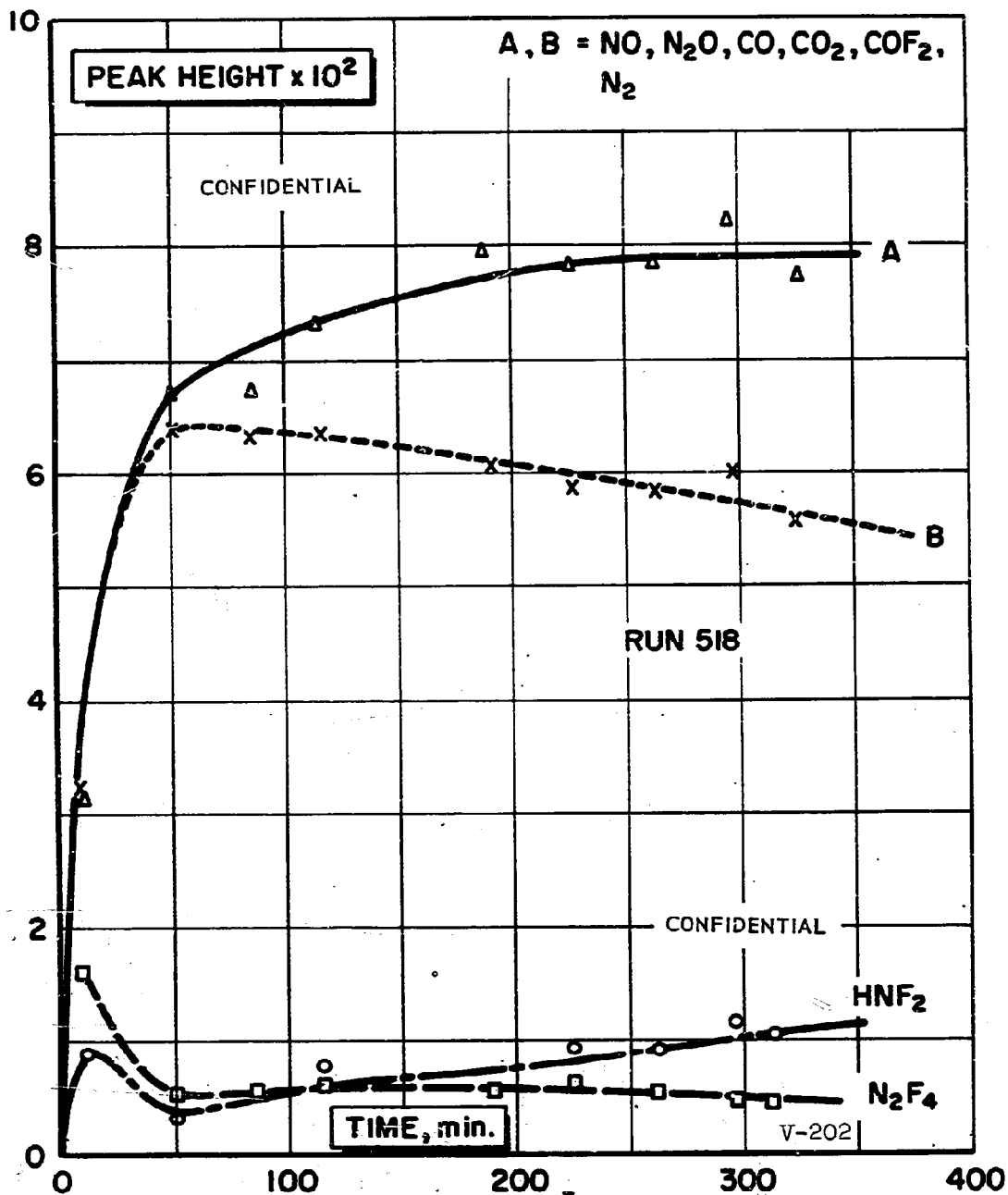
(U) Fig. 3 - Relative Concentration Curve of First Four Peaks
of Chromatographed Gas Samples from Run 518 at 170°C. in Monel
Reactor.

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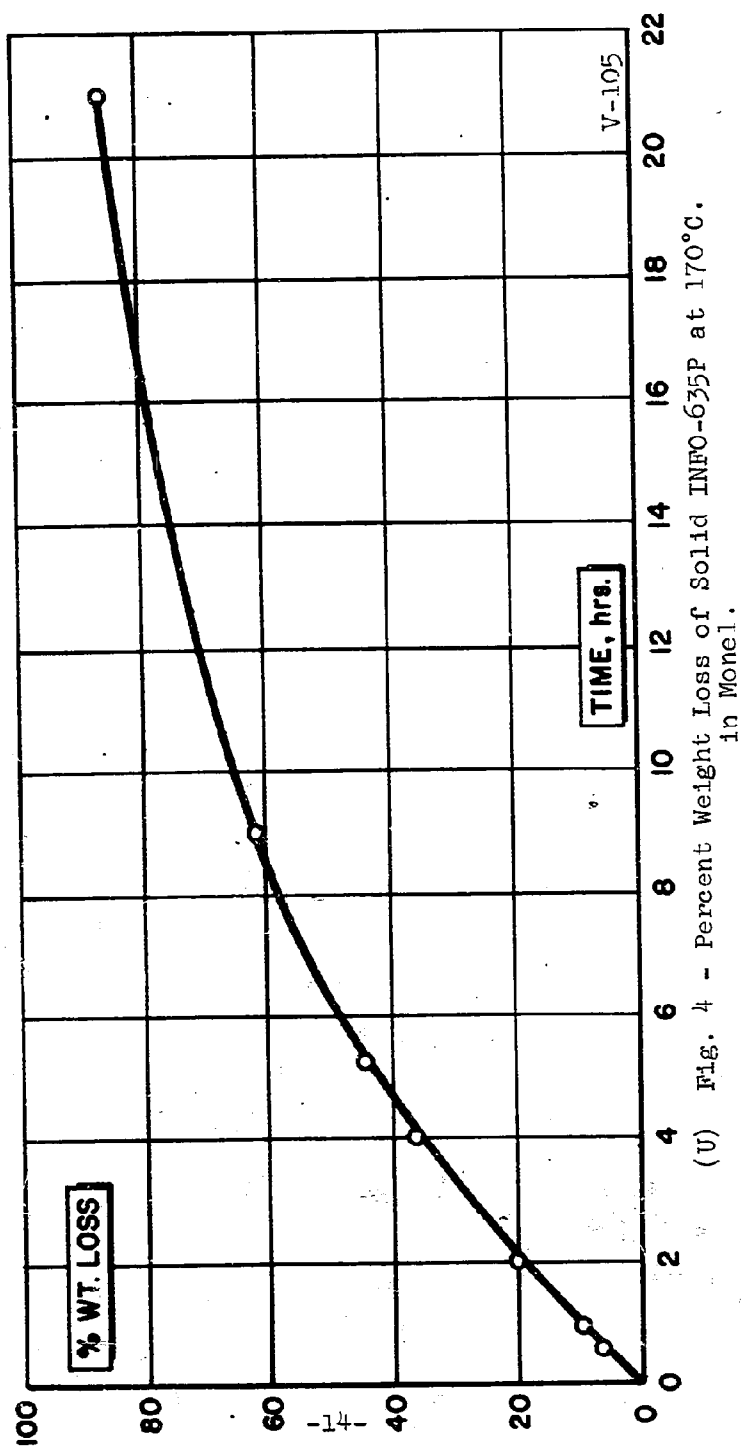
(U) Fig. 4 - Percent Weight Loss of Solid INFO-635P at 170°C. in Monel.

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attached to the vacuum decomposition system so that small amounts of gas products could be sampled through a needle valve while maintaining the vacuum over the solid cryogenically and mechanically.

Table I

(U)   Mass Spectral Results of Decomposition of INFO-635P
in Monel Reactor at 170°C. in Vacuo

Run No.	Time, hrs.	Resulting Compounds Mole Major Product/Mole INFO-635P						
		NO	N_2O	NO_2	CO_2	H_2O	N_2F_2	N_2F_4
628	1	0.003	0.024	0.003	0.057	0.035	0.003	0.024
630	2	0.049	0.041	0.009	0.170	0.018	0.031	0.074
76	4	0.102	0.088	0.020	0.351	0.020	0.068	0.177
726	9	0.25	0.123	0.017	0.703	--	0.047	0.276
728	21	0.271	0.081	--	0.991	--	0.106	0.480

(U)   The principal reason for performing these experiments was to obtain a qualitative picture of the decomposition with respect to the gas phase. No quantitative correlation among the several runs could be made since no standard cracking patterns of the various compounds on this instrument were taken; therefore, as the higher mass fragments begin to appear the distinction between those lighter fragments due to the thermal decomposition and those due to the cracking pattern of the higher masses became more difficult.

(U)   Even a complete intra-correlation of the ion intensities between different spectra of the same run could not be attempted over the entire time range because of the change in the sensitivity factor as the optimum operating pressure of the instrument was exceeded.

(U)   Six decompositions were run in the temperature range 150°C. to 185°C. A representative spectrum at the various temperatures at approximately the same time were taken.

(C)   Analysis of these spectra with respect to mass numbers 20, 36, 47, 52 and 53 was made and the ion intensities were plotted as a function of time (Figures 5 and 6). The most significant point of the reaction at 150°C. is that mass 52 (NF_2) and mass 53 (HNF_2) appear to have reached a steady state (Figure 5). Mass 47, assigned to N_2F from N_2F_2, is steadily increasing. Hydrogen fluoride is by far the most abundant species. Mass numbers 28 and

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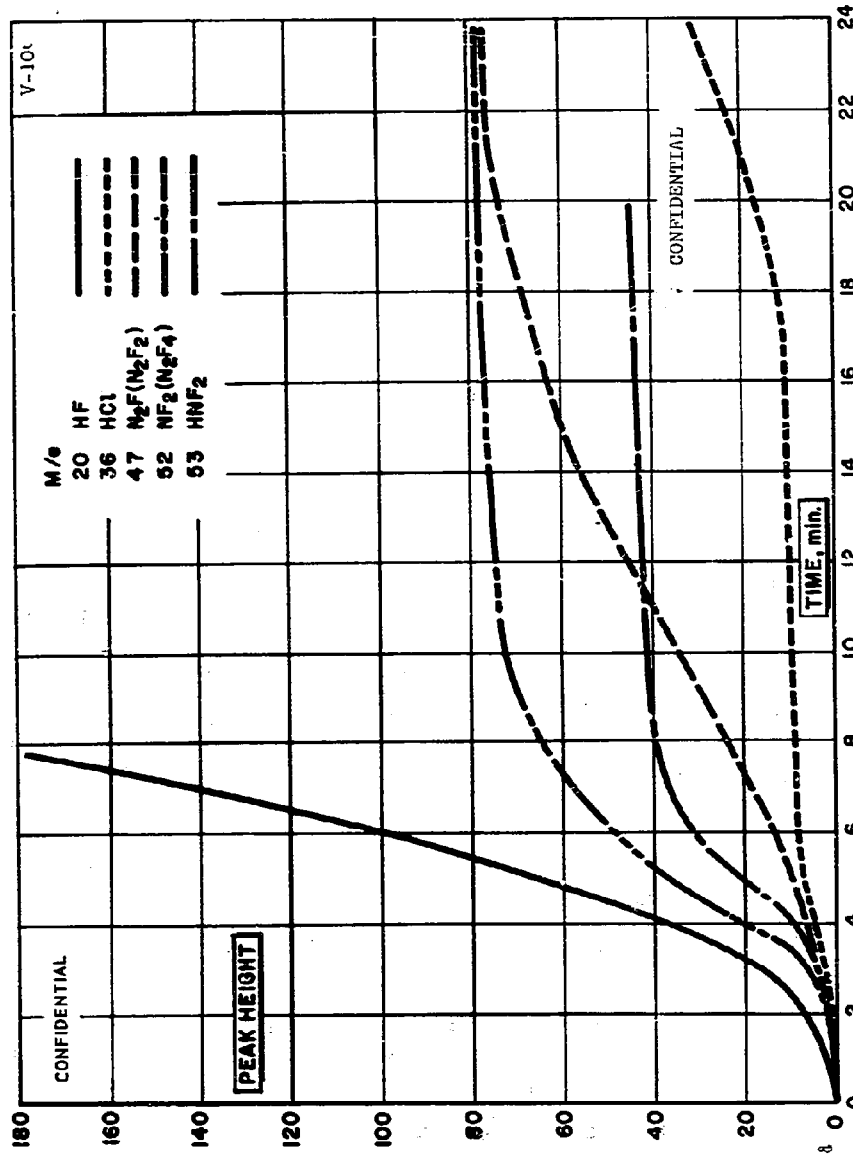
Fig. 5 - Mass Spectral Peak Height as a Function of Time of Selected Gaseous Products from Vacuum Decomposition of INFO-635P at 150°C., in Monel.

(U)
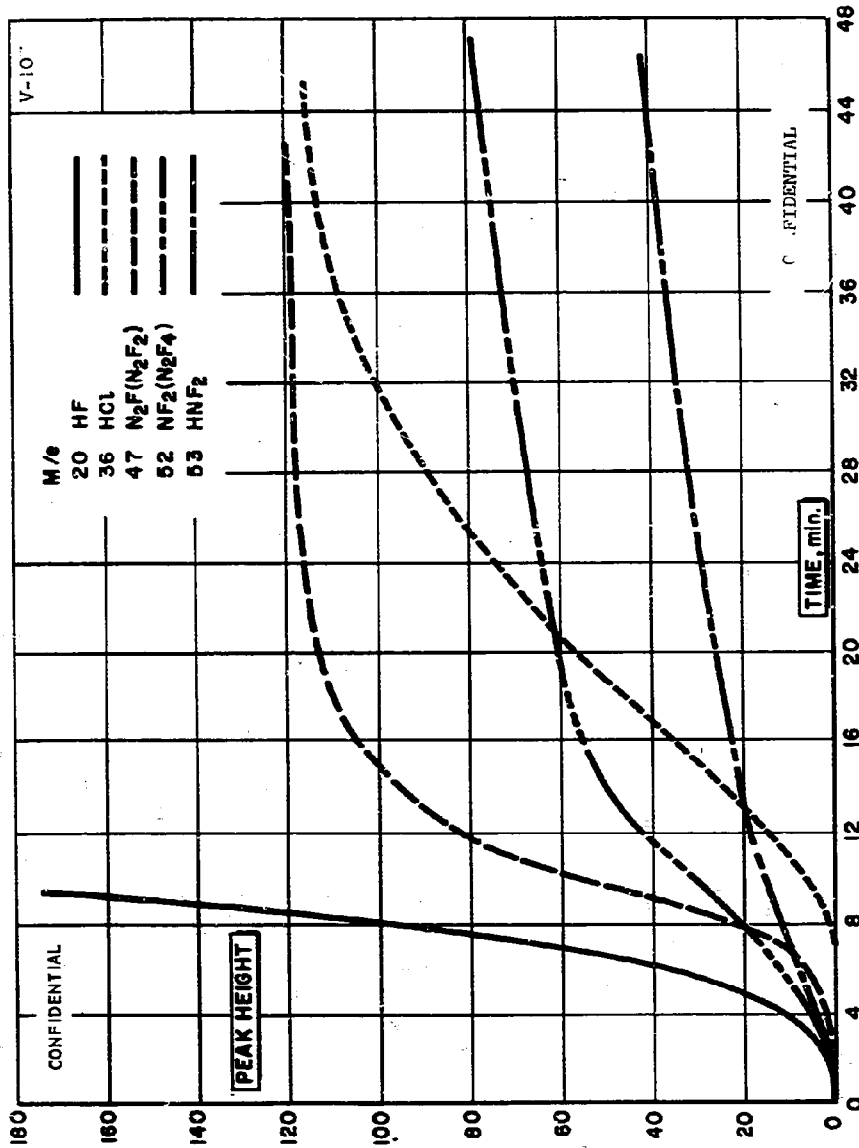
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Fig. 6 - Mass Spectral Peak Height as a Function of Time of Selected Gaseous Products from Vacuum Decomposition of INFO-635P at 170°C., in Monel.

(U)

44 are very abundant and follow similar curves. From high resolution mass spectral data at 120°, 150°, and 160°C., mass 28 and 44 are predominantly -CH$_2$NH$_2$ and CH$_2$CH$_2$NH$_2$ (1).

(C) Figure 6 represents similar curves of the data derived from the decomposition at 170°C. and agrees with the 150°C. run, Figure 5, except that N$_2$F$_2$ (M/e = 47) has also reached a steady state. Hydrogen fluoride is again the predominant species.

(C) The higher mass fragments are observed at longer times. Mass numbers 228 and 168, corresponding to the free amine and (NF$_2$)$_3$C-, indicate that sublimation is an important factor in the decomposition under these vacuum conditions.

(C) The various oxides of chlorine, ClO$_x$, corresponding to the HClO$_4$ cracking pattern, are also observed; however, their relative intensity is not very great during the reaction period, suggesting that the perchloric acid has reacted in some way either with the solid or the metal system.

c. Continuous Vacuum Decomposition of INFO-635P in Glass
   Apparatus (U)

(C) The vacuum decompositions of INFO-635P that were monitored with a mass spectrometer suggested that the oxidizer was partially subliming. Evidence supporting this premise was the observation of the high mass numbers 228, and 168, and the identification of mass 44 and 30 as the ethyl and methyl amine fragments. These results gave rise to the postulation of a series of complex reaction steps involving sublimation, gas phase decomposition, gas-gas reactions, gas-solid reactions, and solid phase decomposition.

(U) The extent of the solid phase decomposition and of the sublimation was not known. Accordingly, an attempt was made to separate and/or minimize the various reaction sequences. Several experiments were run in an apparatus designed such that it could accommodate seven samples at one time. The oxidizer samples were weighed into Teflon cups and placed in a glass reactor. A vacuum was maintained mechanically over each sample simultaneously during each run. The advantage of such a system was that the environment of each sample during any one run was constant, thus minimizing the error due to variation of the external parameters.

(C) A number of vacuum reactions were run from 165°C. to 180°C. The residues of these experiments were all analyzed: first, for total weight loss and then by NMR to determine the amount of INFO-635P remaining in the solid residue, which would allow the calculation of the solid phase decomposition kinetic parameters. Specifically, the tris group of INFO-635P, (NF$_2$)$_3$C- , which yields a single fluorine peak or signal, was used to measure the amount of original material present in the residue, the tacit assumption being that the tris group is present only as INFO-635P and as no

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other solid compound. The solid residues were weighed into the
NMR tubes and kept dry until the spectrometer was ready for use,
then either a 0.5 cc. of 0.1 N $HClO_4$ or a 0.5 cc. of 0.1 N $HClO_4$
plus 10% CF_3COOH, as an internal standard, was added. As an added
precaution to minimize secondary solution decompositions, the loaded
tubes were kept at dry ice temperatures until just before loading
the sample in the NMR. Table II lists the results from one such
run. In each sample set a standard of pure INFO-635P, m.p. 223°C.,
was included. The quantitative result was based upon the ratio of
unknown peak height to standard peak heights or upon the ratio of
their integrals. In either case, the results are consistent. The
data are interesting, suggesting that the residue is essentially
100% INFO-635P. This was confirmed by infrared spectroscopy of
the residue, which gave a spectrum consistent with the pure mate-
rial, and a crude shock test of the residues, all of which ex-
ploded on impact.

Table II

(U)   Comparative NMR Data of INFO-635P Residue
Decomposition at 165°C. in Vacuo

Sample	Time, hrs.	With Internal CF_3COOH Std.		Without CF_3COOH Peak Ht. % INFO
		Peak Ht. % INFO	Integrals % INFO	
1	0.5	93	92	92.5
2	1.5	96	103	106
3	2.5	102	102	102
4	3.5	99	98	95
5	4.5	105	103	--
6	5.5	168[a]	161[a]	--
7	6.5	99	100	--

[a] Residue weight very small; results inconclusive.

(U) During heating of the samples a white solid collected in
the cold zone of the reaction above the oil level and was identified
by infrared spectroscopy as INFO-635P. This sublimed material was
collected from each sample and weighed. This information when
correlated to results on the solid residue shown (Table III) that
at 165°C. about 90% of INFO-635P is recovered. This value de-
creases progressively to 75% for the 180°C. run. Gas products were
also obtained, but these were not collected in a manner that would
give quantitative results.

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Table III

(U) Mass Balance of Solid Material Recovered
from Decomposition at 165°C. in Vacuo

Time, hrs.	Residue Wt., %	INFO in Res., %	INFO Subl.,%	Total INFO, %
0.5	96.45	89.69	1.65	91.3
1.5	81.87	78.59	12.41	91.0
2.5	67.25	67.25	19.80	87.0
3.5	53.04	52.51	40.99	93.5
4.5	30.32	30.32	58.29	88.6
5.5	11.45	~10.0	78.32	89.0
6.5	14.13	13.98	76.69	90.6

(C) All these data imply that there is no solid phase de-
composition, and that decomposition occurs in the gas phase. In
addition, nucleation of the solid, proton transfer forming the
free amine and perchloric acid, and desorption of these materials
from the unreacted solid precede the recombination and condensa-
tion as the salt in the cold zone. Amine salts, under thermal
influence, have been shown to dissociate by proton transfer to
the free amine base and perchloric acid (23).

(C) The linear plot of the amount of INFO-635P remaining in
the residue as a function of time, Figure 7, suggests a zero order
reaction, i.e., the rate of sublimation is independent of the
amount of material present.

$$\frac{dI}{dt} = k \qquad (1)$$

The rate constants and the activation energies were derived by the
method of least squares. The half-life for such a reaction order
is dependent on the concentration of the material present.

$$t_{1/2} = \frac{I_o}{2k} \qquad (2)$$

Therefore, any change on the amount of INFO-635P initially present
in the reactor would affect the half-life and, thus, the slope of
the line. The problem now is whether or not this is a "true" zero

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ZERO ORDER

$$-\frac{dI}{dt} = k$$

$E_a = 38.7 \text{ kcal}$

$$\% = \frac{I}{I_o}(100)$$

165°

180°   170°

TIME, hrs.

V-203
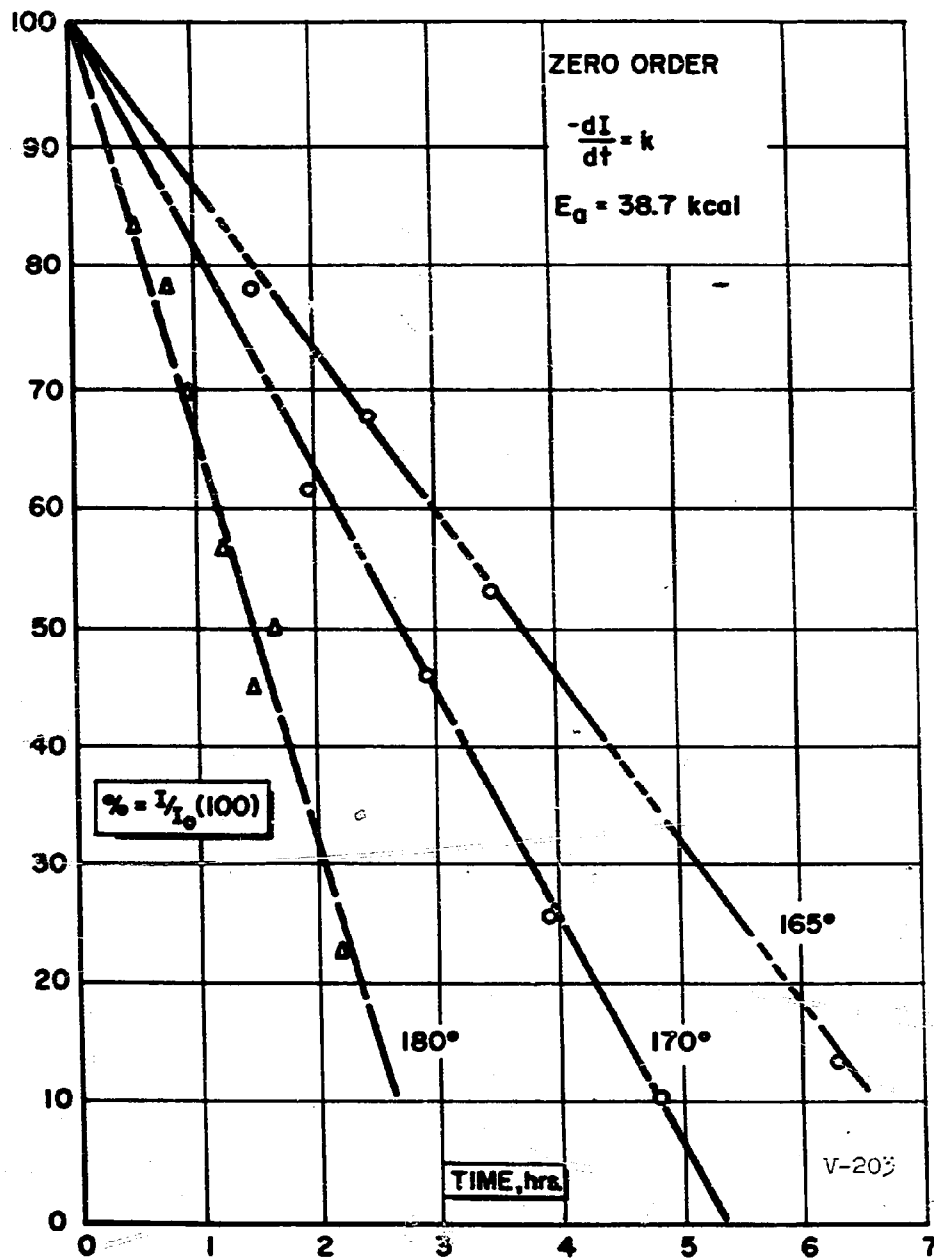
(U) Fig. 7 - Percent INFO-635P Present in Residue

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order reaction. One sample of the 165°C. run was loaded with 45% more INFO-635P than the others. Examination of the data at 6.5 hours (Table III) shows that there is less percentage weight loss and sublimation even at this longer time, implying that this is a "true" zero order reaction. On the other hand, it is commonly assumed that rates of vaporization or sublimation must certainly be a function of the surface area and concentration. In conjunction with this is the knowledge that the reactant vapors, $(NF_2)_3-COCH_2CH_2NH_2(g)$ and $HClO_4(g)$, are forced by mechanical means to flow through a cylindrical element of the reactor. The dependence of the mass transfer upon the mechanical pumping rate is shown in Figure 8, where the log of the weight of INFO-635P sublimed as a function of time is shown to be independent of the temperature. The data plotted in Figure 7 are thus for a "pseudo" zero order reaction.

d. Vacuum Decomposition in Closed Glass System (U)

(U) The results show that under a continuous vacuum extensive sublimation may occur without solid phase decomposition, but with some gas phase decomposition. The experimental system was modified to collect gaseous products cryogenically in a calibrated volume which would allow a more quantitative mass balance determination. The system was designed to allow the cylindrical volume, or hot zone, through which the vapors must past before they reach the cold zone, to be varied from 25 mm., 65 mm., and 155 mm. in length.

(U) All reactions were run at 170°C. and under an initial vacuum of 0.5 micron. A gas pressure increase was observed after long heating cycles in most cases which was due to the non-condensable product gases. Reaction times were held constant at 1, 3, 5, 8 and 19 hours.

(U) The first series of reactions were run at the 25 mm. immersion depth. The data are presented in Table IV. The results are consistent in that a concurrent plot (Figure 9) indicates that there is a direct relationship between the weight lost and the weight sublimed, and that the line follows the theoretical line expected had there been no vapor decomposition.

(C) Run number 1128 (Table IV) was made under one atmosphere of helium to determine whether the sublimation could be prevented, thereby minimizing the gas phase decomposition in favor of a solid phase reaction. This was partially accomplished, since no solid sublimate was observed, but rather a condensable liquid was found which had a vapor pressure and could be transferred in a vacuum. Accordingly it was studied by mass spectrometry at room temperature, but only after most volatiles were removed by fractionation and pumping through the time-of-flight mass spectrometer. The gaseous products were mainly N_2F_4 and SiF_4. The mass spectrum of the liquid (Table V) suggests that the sample has a very high vapor pressure because four masses blanked out the galvanometer of lowest sensitivity. It is also evident that this material is largely the
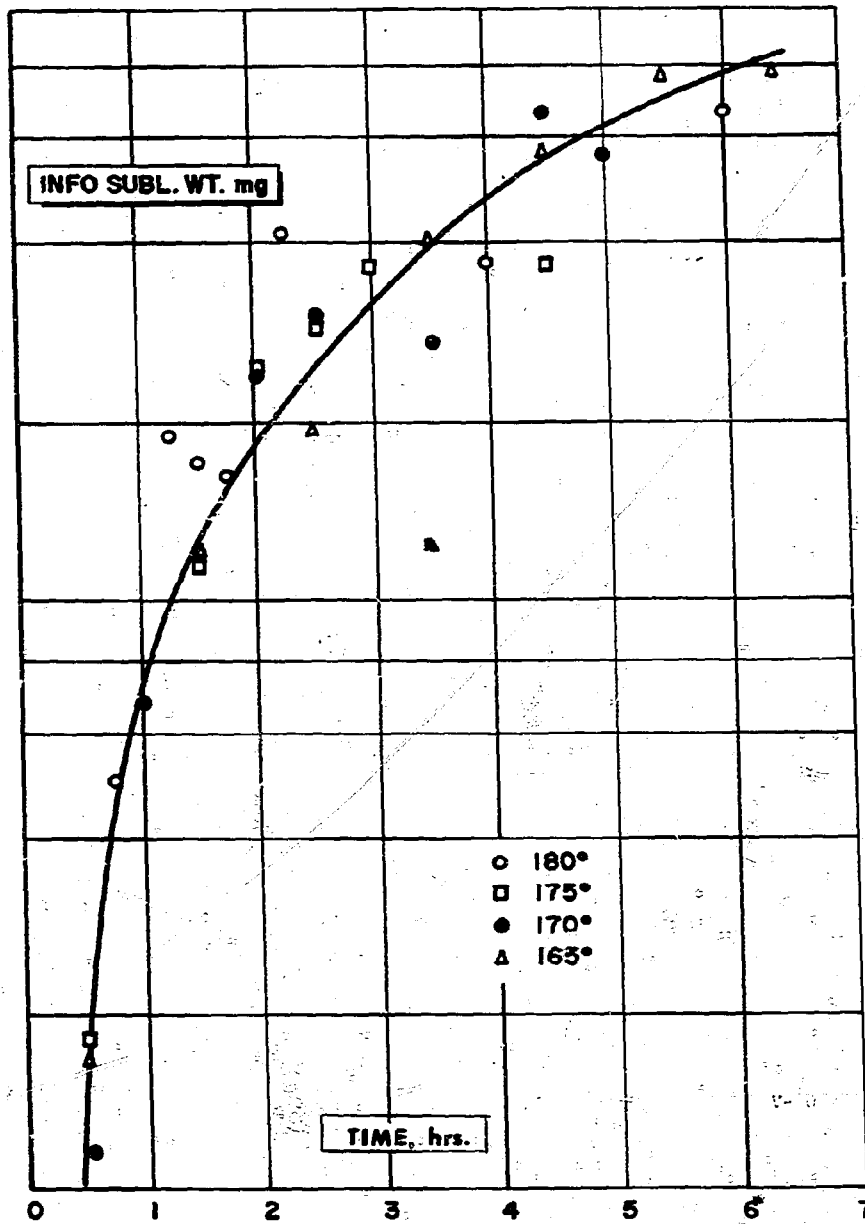
(U) Fig. 8 - Weight of INFO-635P Sublimed Under Continuous Vacuum in Glass Apparatus

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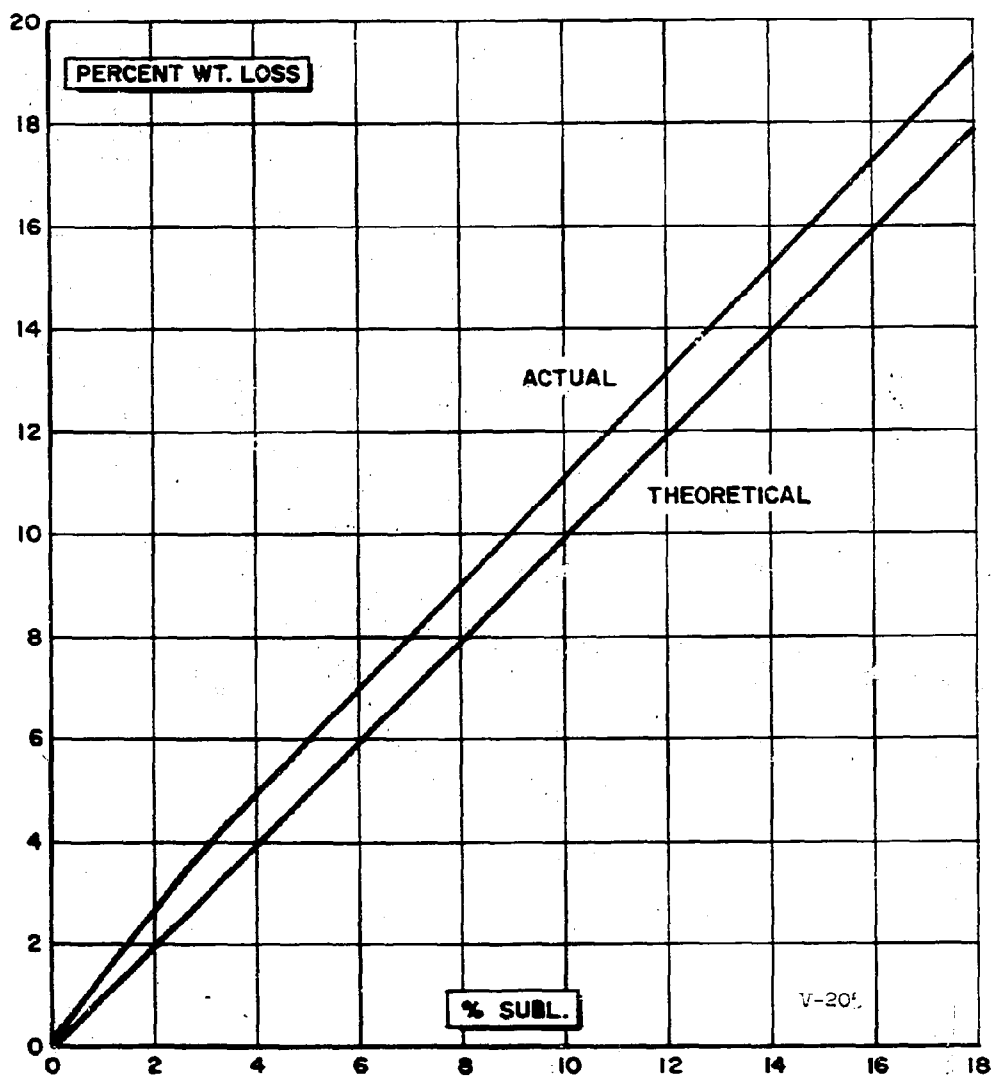
(U) Fig. 9 - Concurrent Plot for INFO-635P; Percent
Weight Loss vs. Percent Sublimed, 25 mm.
Immersion, 170°C.

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free amine, $(NF_2)_3COCH_2CH_2NH_2$, with possibly some small amount of the perchlorate. These results imply that even under one atmosphere of pressure proton transfer has occurred and the free amine has a higher vapor pressure than the perchloric acid, and is capable of diffusing to the cold zone without complete decomposition. However, there was approximately 91% weight loss.

Table IV

(U)   Mass Balance of INFO-635P Decomposition
at 25 mm. Immersion Depth at 170°C.
and in Presence of Non-condensable Gases

Nr.	Time, hrs.	Org. Wt., mg.	% Lost	% Subl.	% INFO Decomposed
126A	1	80.5	1.74	1.24	0.5
126P	3	81.1	6.55	5.55	1.0
127	5	80.8	9.40	7.92	1.48
129	8	81.8	19.30	18.08	1.22
1157	19	84.9	45.35	37.46	7.89
1125	19	91.7	55.07	50.70	5.37
1128[a]	19	83.1	91.21	(Liq.)	---

[a]Helium at one atmosphere.

(U)   This same series of experiments was repeated except that the immersion depth was increased to 65 mm. Table VI lists the weight balances.

(U)   A plot of the log percent weight remaining as a function of time (Figure 10) reveals that when mechanical pumping is eliminated the disappearance of INFO-635P follows a first order rate law. A concurrent plot (Figure 11) again shows a linear relationship between the weight loss and the weight sublimed to about 50% weight loss, where the rate of weight loss accelerates, probably because of increased pressure of the non-condensable gases or of a catalytic effect of one of the products. The difference in the slope of the linear portion of the experimental line from the theoretical line (Figure 11) is a measure of the rate of gas phase decomposition.

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Table V

(C) Mass Spectrum of Condensable Liquid from Run 1128
in Order of Decreasing Intensity

M/e	Possible Assignment	M/e	Possible Assignment
85*	N_2F_3, SiF_3	28	N_2, CO
43*	CH_3OC, C_2F	66	N_2F_2, SiF_2
63*	CH_3OCHF	47	N_2F, OCF, CCl, SiF, CH_2F
27*	C_2H_3, HCN	52	NF_2
29	CHO, CH_3N	31	CH_3NH_2
44	$CH_2CH_2NH_2$, CO_2	124	$(F_2N)-C-OCH_2CH_2NH_2$
67	$Cl^{35}O_2$	168	$(F_2N)_3C-$
30	CH_2NH_2	104	N_2F_4
69	$Cl^{37}O_2$	181	$(NF_2)_2COCH_2NH_2$
33	NF		F

*High Intensity.

Table VI

(U) Mass Balance of INFO-635P Decomposition at
65 mm. Immersion Depth at 170°C.
and in Presence of Non-condensable Gases

Nr.	Time, hrs.	Org. Wt., mg.	Percent Lost	Percent Subl.	Percent Decomposed	Decomposed, mg.
126A	1	81.2	16.4	15.1	1.3	1.0
126P	3	81.5	32.6	29.7	2.9	2.4
137	5	84.0	44.4	39.0	5.4	4.5
129	8	82.2	61.8	51.7	10.1	8.3
1117	19	77.4	85.01	60.98	24.0	18.6

(C) The composition of the gaseous products collected from the above series of reactions was quantitatively determined by mass spectrometry. The data are given in Table VII in units of moles of gas per mole of original INFO-635P. There is a large percentage difference in the mass balance of the weight decomposed versus weight of gases recovered (last column Table VI and VII). However, the actual difference in the first three runs after correcting $SiF_4(g)$ to HF(g) is less than 0.8 mg. A plot of the moles

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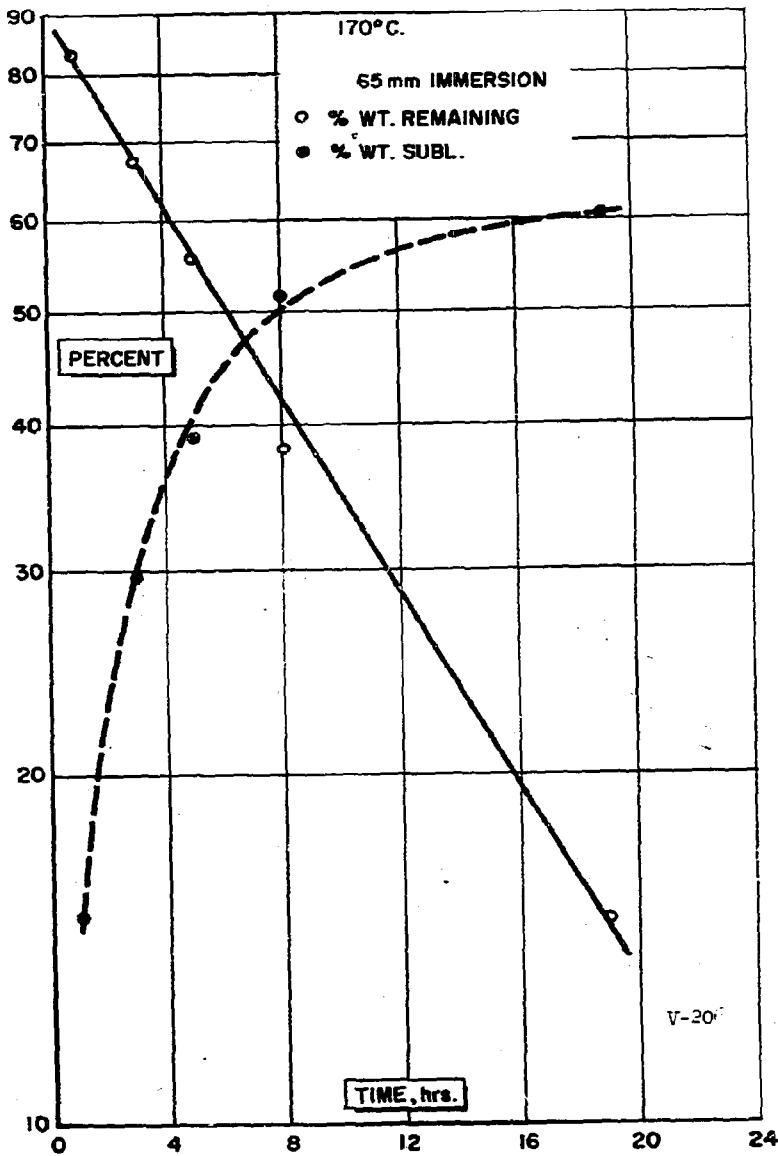
(U) Fig. 10 - First Order Plot INFO-635P Decomposition,
170°C. 65 mm. Immersion

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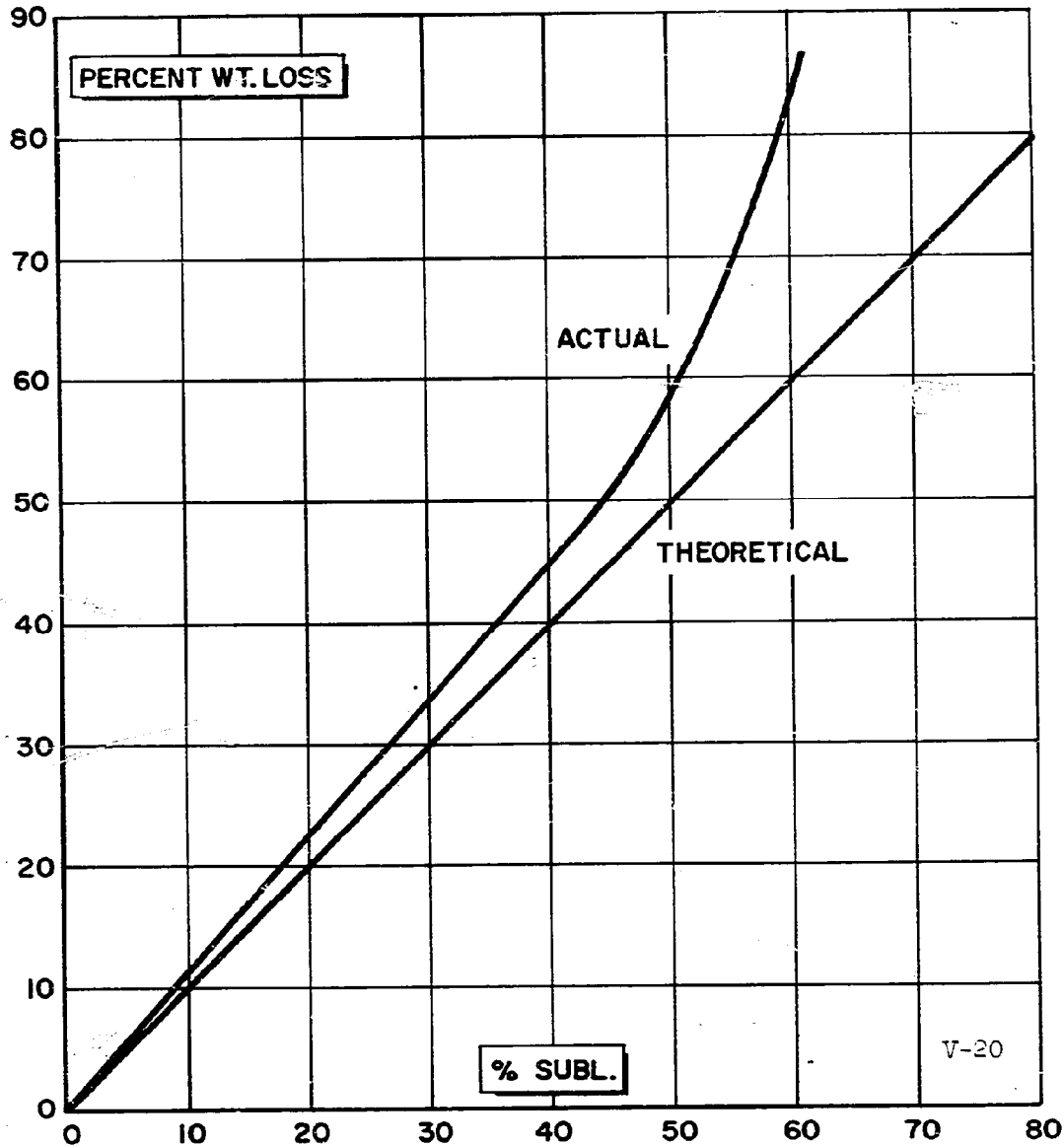
(U) Fig. 11 - Concurrent Plot for INFO-635P; Percent
Weight Loss vs. Percent Sublimed, 65 mm.
Immersion, 170°C.

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of gas per mole of original INFO-635P also shows a remarkable smooth line which is indicative of the correctness of the relative concentrations (Figures 12 and 13).

Table VII

(C)   Mass Spectrum of Product Gases from 65 mm. Immersion Runs at 170°C.

| | Run Number | | | | |
	126A	126P	127	129	1117
Time, hrs.	1	3	5	8	19
Moles gas/ mole INFO-635P- x 10⁻²					
N_2	1.81	4.40	5.90	9.08	8.66
NO	0.197	0.717	1.33	1.46	8.57
N_2O	0.083	1.02	1.32	1.77	7.43
CO_2	0.544	3.11	6.77	6.54	26.8
N_2F_4	0.328	1.81	3.53	4.38	13.9
N_2F_2	0.329	2.18	3.90	5.60	10.95
HNF_2	0.094	0.133	0.303	1.46	0.891
SiF_4	0.328	1.38	2.92	4.21	10.2
C_2F_4	0.05	0.101	0.137	--	--
Wt. gas, mg.	0.453	2.28	3.92	5.12	12.8

(C)   There is a correlation between the stoichiometry of two decompositions, shown in Table VIII, where the coefficients are expressed as moles of gas per mole of INFO-635P decomposed. The weight of INFO-635P decomposed was assumed to be the weight lost as gases (last column Table VII).

Table VIII

(C)   Stoichiometry of Gas Phase Decomposition, 65 mm. Immersion, 170°C., moles gas/mole INFO-635P decomposed

Run Nr.	N_2	NO	N_2O	CO_2	N_2F_4	HNF_2	N_2F_2	HF	C_2F_4
126P	1.6	0.27	0.30	1.2	0.67	0.05	0.80	2.05	0.04
127	1.1	0.25	0.25	1.3	0.66	0.05	0.73	2.18	0.03

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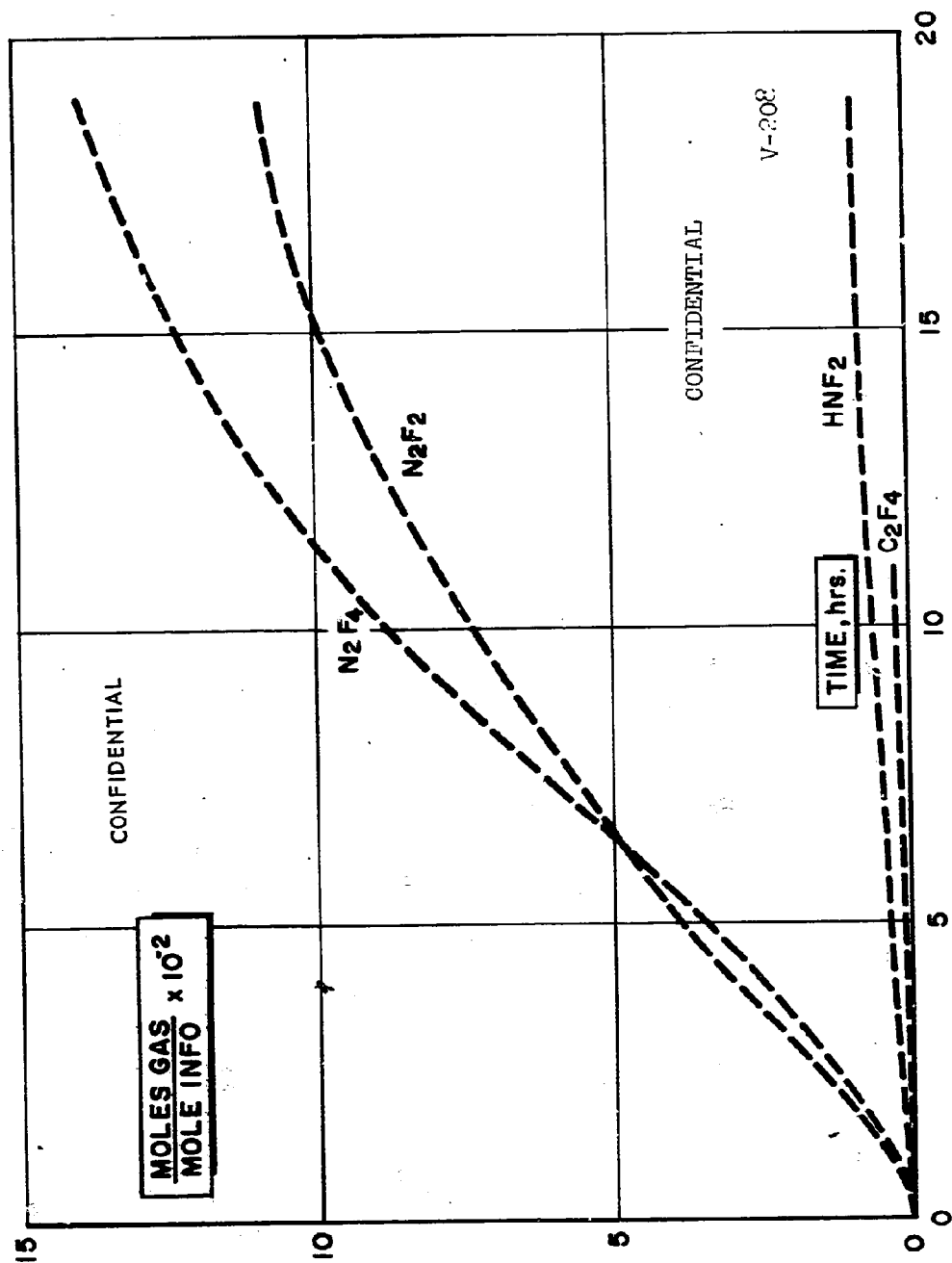
(C) Fig. 12 – Product Gases I, INFO-535P Decomposition At 170°C., 65 mm. Immersion

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(C) Fig. 13 - Product Gases II, INFO-635P Decomposition
At 170°C., 655 mm. Immersion.

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(C) The total moles of nitrogen and fluorine exceed the theoretical value of 2 and 3 moles, respectively (Table IX). A rationalization of this discrepancy is described in the following paragraph.

Table IX

(C) Elemental Mass Balance of Decomposition
at 170°C., 65 mm. Immersion

Nr.	Time, hrs.	Units, Moles/Mole INFO-635P Decomposed					
		N_2	F_2	C	O_2	H_2	Cl_2
126P	3	3.55	3.29	1.22	1.47	1.05	--
127	5	2.88	3.24	1.31	1.51	1.12	--
Theory	--	2	3	3	2.5	3.5	0.5
127[a]	5	6.59	7.41	3	3.45	2.55	--

[a]Normalized carbon to ideal value.

(C) If the assumption that the weight lost, after accounting for the weight of sublimed INFO-635P, is correct and that decomposition is in the gas phase, then two alternatives are available. If the total moles of nitrogen (N_2) and fluorine (F_2) recovered as a gas are correct, some material containing about one-half the available C, H, O, Cl is missing. If the C, H, O, values are correct, then the N_2 and F are in excess. In conjunction with this, the appearance of the solid residue must be considered. In all the runs, except the one hour decomposition, the solid residue had discolored, suggesting that the solid does decompose or react. Thus, the initial statement that decomposition is only in the gas phase is not entirely correct. The residue, however, is still composed mainly of unreacted INFO-635P. If the total moles of carbon recovered is normalized to the theoretical value of 3, and the correction applied to the other elements, the total amount of N_2 and F_2 are greatly in excess. The excess, however, is in a 1:1 mole ratio, which leads to the conclusion that, under vacuum conditions and concurrently with the sublimation process, some sort of solid phase reaction or decomposition is initiated involving the tris-NF_2 group and HF formation involving fluorine abstraction. The process is slow relative to the sublimation, but, as the pressure over the solid is increased, the rate is increased and the reaction becomes a great deal more complex.

(C) Several reactions were made at 180°C. in an attempt to duplicate the general results of the 170°C. runs to derive an activation energy, E_a, for the sublimation. However, the present

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results duplicated the earlier experience of decomposition at
180°C. in the monel reaction, i.e., that the decomposition is very
fast, almost explosive. The present data, (Table X, XI) show that
there is more than one path by which INFO-635P may be nucleated and
decomposed. The one path which is the "slow" reaction leads to the
expected formation of the various NF_2 compounds. The second path,
which is a very fast decomposition as determined by the rate of
pressure increase, leads to a slight increase in N_2F_2 concentration,
a markedly increased N_2O concentration, and no detectable NF_2 com-
pounds (Figure 14).

Table X

(C)   Weight Balance INFO-635P Decomposition at 180°C.
65 mm Immersion

Time and Weight Balance	Run Nr. 1216	1217	1219
Time, hrs.	3	8	8
Org. wt., mg.	82.4	82.9	80.9
Wt. lost, mg.	33.1	75.9	53.6
Wt. lost, %	40.2	91.6	66.3
Wt. subl., mg.	21.2	--	25.4
Wt. subl., %	25.7	--	31.4
Wt. decomp., mg.	11.9	75.9	28.3
Wt. rcvd.[a] gas, mg.	7.9	75.7	19.1
Final press non-cond. gas, mm.	1.4	55.0	3.2

[a]Wt. gas corrected SiF_4 to HF.

4.   **Decomposition of INFO-635P in the Presence of Product Gases, in Monel Reactor (U)**

(U) A lack of reproducibility was observed with the pressure-
time reactions in the monel reactor. These inconsistencies
(Figure 15) among similar runs of INFO-635P were believed to be
the result of non-uniform crystal size. Attempts to minimize this
incongruity by depositing a thin film showed that the decomposition
was too fast for kinetic sampling of the products, probably be-
cause of self-heating. The reproducibility of the experiments
improved by sieving the solid into batches with a narrow range of
particle size. Induction periods, where present, were decreased by
increasing the surface area, in this case by sieving. The reactions
using sieved samples were more controllable and were used in all
subsequent experiments.

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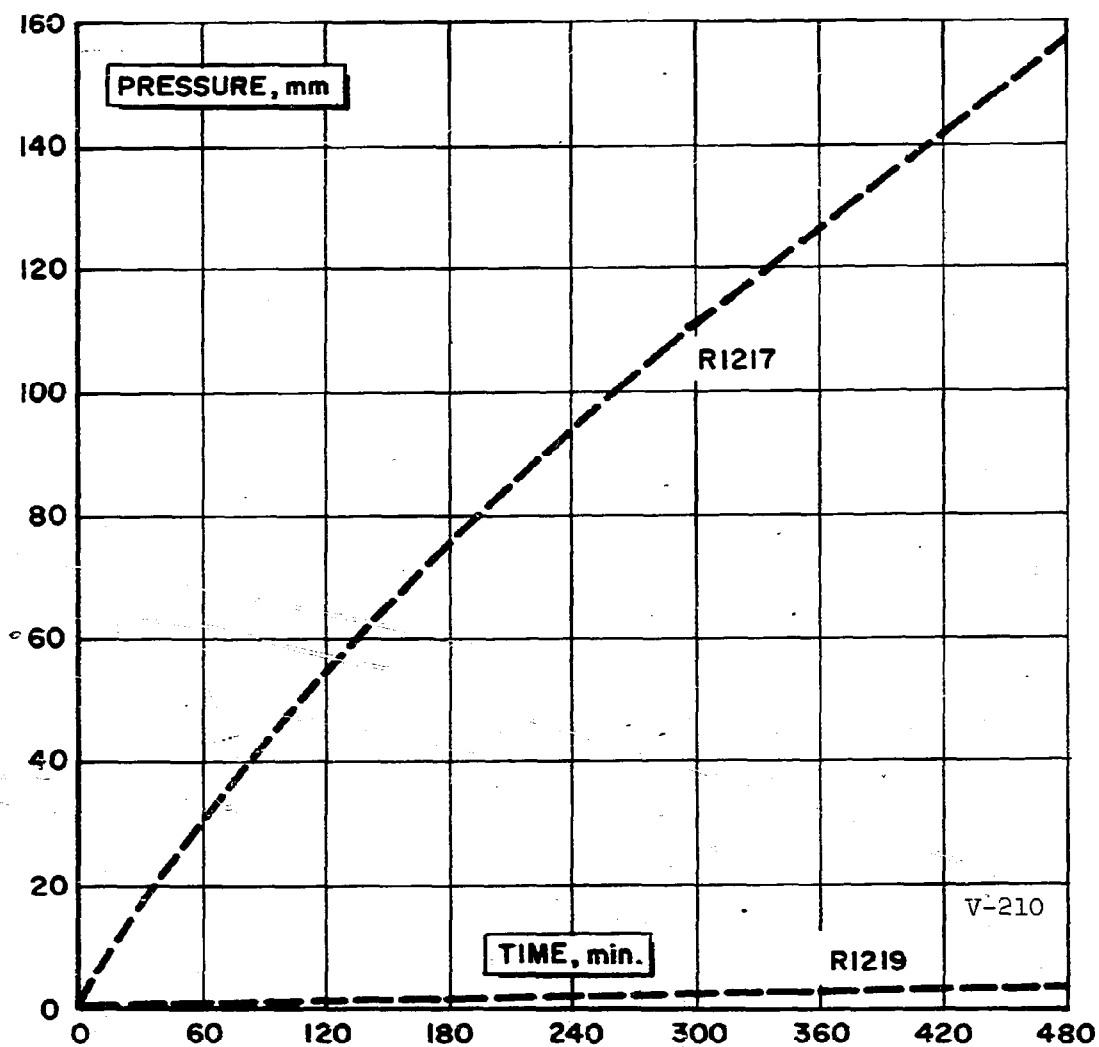
(U) Fig. 14 - Total Pressure Non-condensable Gases, INFO-635P
Decomposition 180°C., 65 mm. Immersion.

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RUN	WEIGHT, mg
325	197.0 60 MESH
424	316.3 60 MESH

MOLES GAS / MOLE INFO

TIME x 100, min.

V-211
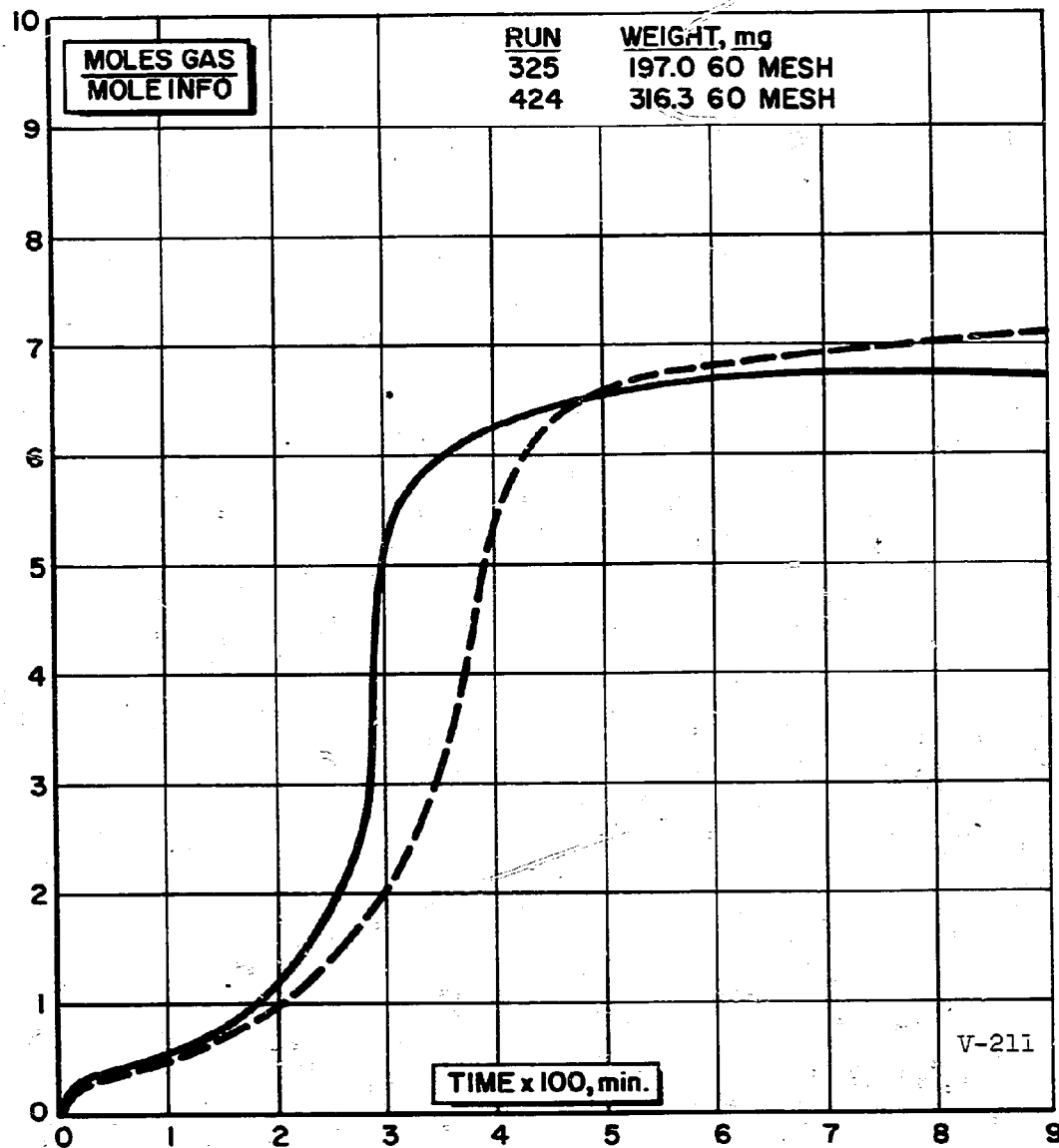
(U) Fig. 15 - Total Pressure-Time Curves for INFO-635P
Decomposition at 160°C. in Monel.

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Table XI

(C) Mass Spectra Gaseous Products from
INFO-635P Decomposition at 180°C., 65 mm. Immersion

Gaseous Products	Run Number		
	1216	1217	1219
mole gas/mole INFO-635P x 10^{-2}			
N_2F_4	10.05	0	20.20
N_2F_2	8.59	5.37	14.89
HNF_2	0.036	0	0
SIF_4	8.77	51.05	16.04
$CNCl$	0.06	1.33	0.14
CO_2	16.26	355.5	42.71
N_2O	1.81	125.0	8.02
NO	7.54	61.84	25.08
N_2	4.56	49.06	13.18
Cl_2HC-CH_3	0.18	1.34	0.43

(U) Since sublimation is an integral part of the decomposition under vacuum conditions, the observed poor reproducibility in the p - t data is now better understood. As was mentioned earlier, the rate of sublimation is a function of the surface area and concentration as well as the temperature and pressure. If this rate is first order, then an increase in the concentration should increase the sublimition rate. Since the monel reactor decompositions were run in a closed system, an increase in the initial concentration would increase the sublimation rate which would then necessarily increase the rate of gas phase reaction.

(C) The stoichiometry determined in earlier decompositions in monel (Table XII) showed an excess of nitrogen and carbon. The difficulty is that the gases analyzed by mass spectrometry are not necessarily the same as those in the hot reactor prior to sampling. Specifically, all the fluorine is not mass balanced whereas most of the carbon and nitrogen is accounted for in the decomposition. The fluorine, as hydrogen fluoride (HF), must have reacted with the collection system in some manner. Also, the calculational units are in terms of moles of product gas per mole of INFO-635P, which implies that all the original material has reacted and is in the gas phase. Actually, there is always a residue; thus, the assumption is not valid. Both of the above points have the effect of increasing the moles of gaseous products. A crude correction for SiF_4 to HF gas, assuming that half the fluorine ends up as HF gas, yields the stoichiometry shown in Table XII for a reaction at 160°C.

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Table XII

(C)   Stoichiometry of 160°C. Decomposition
of INFO-635P in Monel Reactor

Stoichiometry	Gas, moles gas/mole INFO-635P							
	N_2	N_2O	CO	CO_2	SiF_4	CNCl	CF_4	Unknown
Uncorrected	2.04	1.49	1.01	2.72	0.84	0.08	0.01	0.06
Corrected	1.25	0.92	0.62	1.69	2.54[a]	0.04	0.006	0.03

[a]Represented as HF(g).

(U)   Because of the sublimation and the conclusions drawn concerning the total pressure decompositions, a re-evaluation of the p - t data is necessary. First order plots (Figure 16) of the data were again made and the rate constant derived by least squares calculation. The pressure results for the first 30 minutes were ignored in this derivation. An Arrhenius plot of these constants (Figure 17) shows excellent linearity from 175°C. to 160°C. The rate constant, k, from the p - t data at 150°C. was recalculated by extending the range from 100 to 400 minutes. The derived rate constant now fits with the other data points. The activation energy (E_a) derived by least squares is 39.5 kcal. The rate constant derived for the 180°C. decomposition did not fit the curve.

(U)   There is a more general method of analyzing the results from which activation energies can be derived (24). It is based on the assumption that a single kinetic equation is applicable over a specific small range of decomposition independent of the temperature. The rate equation is given the form:

$$F(\alpha) = kt \tag{1}$$

where $\underline{k}$ is the rate constant. The values of fractional decomposition are α_n, α_{n+1}, at times t_n, t_{n+1}.

(U)   Then, over a finite range decomposition:

$$F(\alpha_{n+1}) - F(\alpha_n) = k(t_{n+1} - t_n) \tag{2}$$

and at any different temperature, but the same values of α:

$$F(\alpha_{n+1}) - F(\alpha_n) = k' (t'_{n+1}) = \text{constant}$$
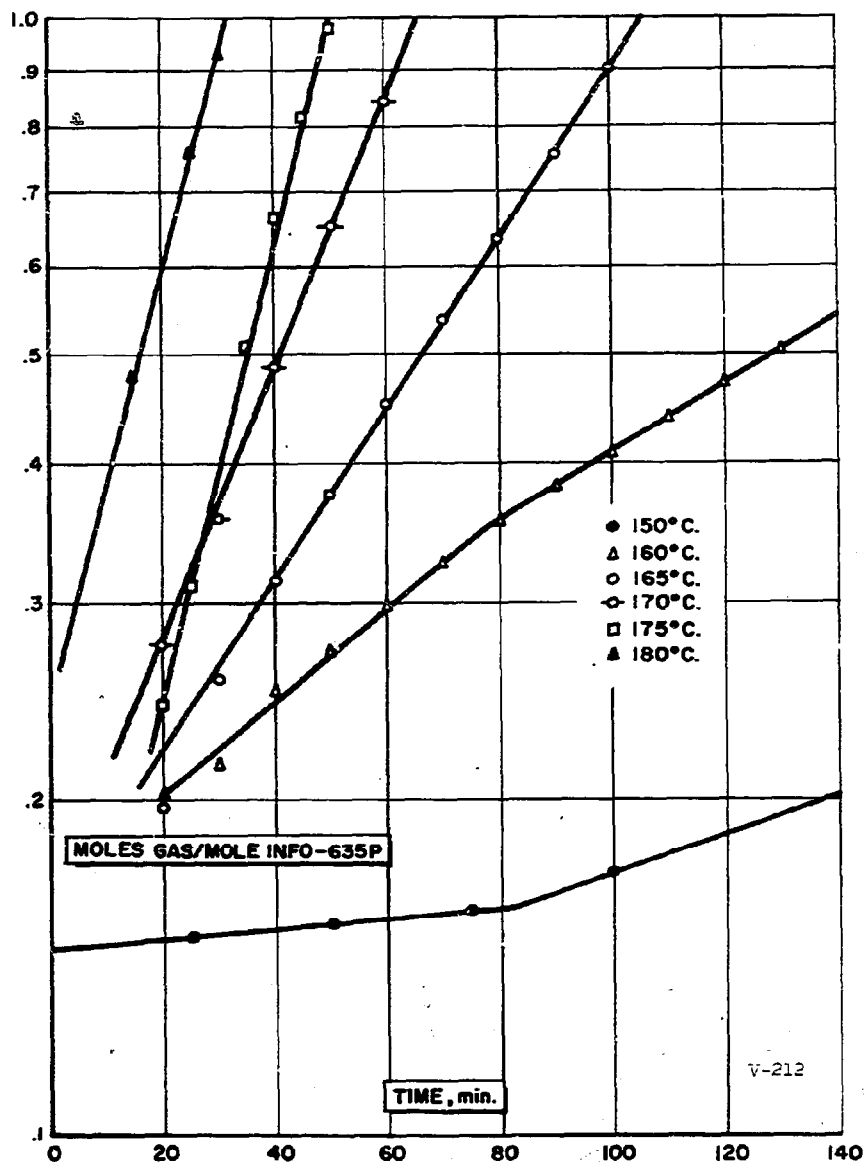
(U) Fig. 16 – Total Pressure-Time Curves for INFO-635P
      Decomposition, Initial Period
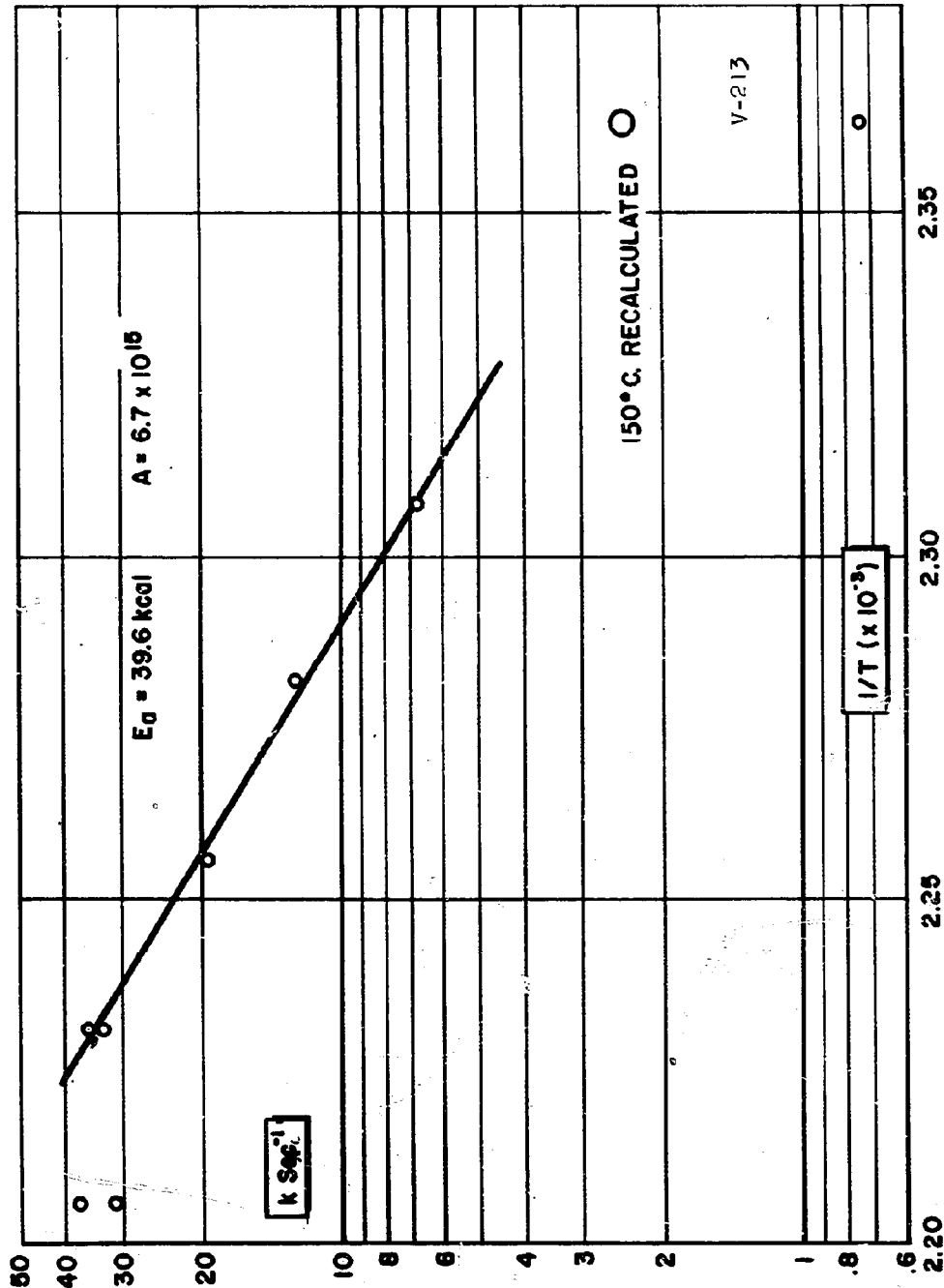
(U) Fig. 17 - Arrhenius Plot From Total Pressure Data INFO-635P Decomposition

From the Arrhenius equation it follows that a plot of log $(t_{n+1} - t_n)$ against $1/T$ is linear with slope $E/2.303\,R$. Since the form of the kinetic equation $F(\alpha)$ is not known, the pre-exponential factor cannot be found.

(U) The fractional decomposition (α) was assumed to be moles of gas produced per mole of INFO-635P originally loaded into the reactor. This is not a measure of the decomposition of the solid; however, based upon information developed from experiments in vacuo, α is believed to be more a measure of gas phase decomposition.

(U) In an earlier report (25) this method was used to derive activation energies for the temperature range 165°- 180°C. and 150°-160°C. A least squares derivation is made in the range 175°-150°C. and in the range $0.25 < \alpha < 1.0$, an activation energy of 45.3 kcal. is derived with a standard deviation of ±2.3 kcal. Since these activation energies are derived from pressure data, their interpretation mechanistically is ambiguous because of the complexity of the total decomposition.

5. Residue Analysis (U)

(C) All the residues from the total pressure reaction from 160°C. to 180°C. in the monel reactor had the same physical appearance and gave the impression that liquefaction had occurred. All samples were orange, and there seemed to be two different substances, one a solid and the other a tacky or amorphous substance. The residue was treated with acetone; the solid portion was insoluble and was set aside for further analysis. The tacky portion was soluble; it was re-precipitated as a pale yellow powder from acetone with ether. It was found not to be shock sensitive; upon heating it began to discolor at about 180°C. and finally decomposed with gas evolution. The resulting residue from this is similar in appearance to the acetone-insoluble material of the original sample. The tacky or amorphous form can be regenerated by dissolving the yellow powder in acetone and then allowing the solvent to evaporate. Infrared analysis of this soluble material suggests the presence of ClO_4^-, $C=O$, or possibly fluorinated $-C=C-$, and possibly a cyclic carbonate structure (Figure 18).

(C) X-Ray analysis of the solid revealed only two crystalline materials, INFO-635P and ammonium perchlorate, along with some amorphous material. Mass spectral results of this material indicate that it may be one or more halogenated substances. Since acetylene and ethylene have been observed in the gas phase by mass spectroscopy, the existence of low molecular weight polymers is very plausible.

(C) The residue from each of the vacuum decompositions in monel was still a powder, in contrast to the total pressure runs where the impression of flow was observed. The color change varied progressively from white to pale yellow to orange as the time of decomposition increased.
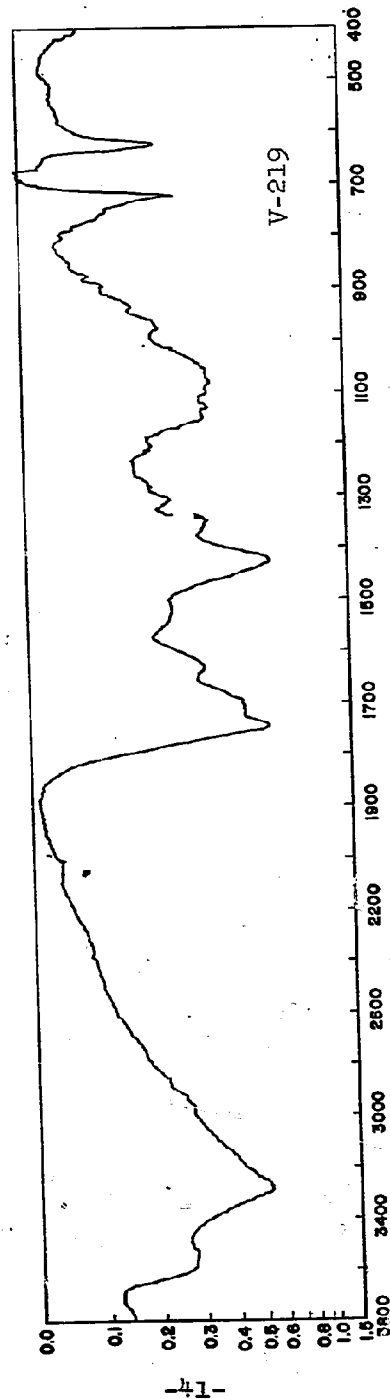
(U) Fig. 18 – Infrared Spectra of Acetone Soluble Portion of Residue

(C) The residue from vacuum reactions at 170°C. in the monel reactor was assumed to contain unreacted INFO-635P and AP as the only ClO_4^- containing compounds. Therefore, quantitative analysis of the residue for total ClO_4^- and $NH_3(g)$ content should give an indication of the rate of disappearance of INFO-635P. The results indicate that there may be at least one other perchlorate in the residue since the total weight of the residue calculated from the ClO_4^- and $NH_3(g)$ content does not balance with the original weight of the residue (Table XIII). NMR analysis of the residue indicates the presence of an aliphatic chain, as well as several other absorptions which could be attributed to the NCH or OCH type of bonding.

Table XIII

(C) Mass Balance of Residue Based Upon Total ClO_4^- and $NH_3(g)$ for 170°C. Decomposition of INFO-635P in Vacuo

Run Nr.	Time, hrs.	Residue Wt., mg.	Mass Balance				
			H_2O Insol. mg.	AP mg.	INFO mg.	Total Wt. mg.	
78	0.5	201.3	0.35	--	200.9	201.3	
628	1.0	193.1	0.24	--	178.4	178.6	
630	2.0	168.4	0.78	3.1	166.2	170.0	
76	4.0	136.0	2.17	3.6	135.4	141.2	

(U) Active fluorine analysis of these residues gave the results shown in Table XIV.

Table XIV

(C) Active Fluorine Analysis of INFO-635P Plus Residues

Run Nr.	Time, hrs.	Fluorine equivalents/mole
Standard	--	5.3
78	0.5	~5.3
630	2	3.7
76	4	4.4

(C) Normally, the number of equivalents would be expected to decrease as a function of time. The data in Table XIV do not

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verify this expectation. This increase in activity is believed due to the formation of NO_2- groups in the residue which can also oxidize I^-.

(C) The residue from Run 723 decomposed in the monel reactor under vacuum after twenty-one hours appeared homogeneous. This material had a melting point of 237°C. with decomposition. Elemental analysis resulted in the following empirical formula $C_{24}H_{43}N_{15}O_{36}FCl_8$. Emission spectroscopy on this sample showed less than 0.17% total metal present.

(C) High resolution mass spectroscopy of this residue at temperatures varying from 130°C. to 230°C. gave essentially the same spectrum as shown in Table XV. As indicated from the mass spectral results, the principal component observed is $HClO_4$ and its related mass fragments. Comparing this mass spectral pattern to the empirical formula indicates that no carbon, hydrogen or nitrogen were observed. The residue could therefore be a complex polymeric amine perchlorate.

(C) Thin layer chromatography of residues from two runs Number 628 at 170°C. for one hour, and 712 at 150°C. for 12 hours, gave the same results. There was one major impurity and one trace component, exclusive of NH_4ClO_4. The major impurity is basic and treatment with ninhydrin indicator gave a deep purple which suggests that it is a primary amine or an ammonium salt, but not NH_4ClO_4 which is not very sensitive to ninhydrin indicator.

(U) In comparison to the glass vacuum system, the monel vacuum was extremely constricted. The gases in the glass system passed through a one inch I.D. tube to the cold trap; the gases in the monel system passed through a 1/32" I.D. hole, 2.5 inches long before entering the vacuum manifold. The residues are therefore contrasted but not inconsistent.

6. Mass Spectrometric Techniques (U)

(C) Mass thermal analysis (MTA) and high resolution mass spectroscopy of the solid decomposition (Figure 19 and Table XVI) suggest that the free amine is formed prior to decomposition. This is based upon the M/e value 44 ($CH_2CH_2NH_2^+$) and M/e value 30 ($CH_2NH_2^+$) observed in the mass spectrum. Considering that the slow thermal decompositions were run at 160°C. and 170°C., the absence of these compounds is understandable because the amines are most likely unstable under these temperatures.

(C) The mass spectra and slow thermal results are obviously different. There are two plausible explanations. Since the temperatures are so different, 120°C. and 170°C., a comparison is being made of the decomposition of the two different crystalline modifications. Under the high vacuum conditions of the mass spectrometer and the low temperatures, INFO-635P was sublimed and the cracking pattern of free amine and perchloric acid was observed.

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At the higher temperature some of the free amine that vaporized from the surface decomposed in the gas phase before entering the ionization chamber of the mass spectrometer.

<u>Table XV</u>

(C) <u>High Resolution Mass Spectrum of Residue</u>
<u>from Run 728</u>

M/e	Assignment
102	$HCl^{37}O_4$
100	$HClO_4$
87	--
85	$Cl^{37}O_3$
83	ClO_3
69	$Cl^{37}O_3$
67	ClO_2
64	--
54	$HOCl^{37}$
52	$HOCl$
53	$Cl^{37}O$
51	ClO
44	--
43	--
38	HCl^{37}
37	Cl^{37}
36	HCl
35	Cl

(U) The double reaction sequence observed in the MTA results (Figure 19) may now be explained as sublimation in the initial period, and as the sample is heated it begins to pre-melt, decreasing the sublimation rate. Continued heating results in total liquefaction, which finally leads to vaporization of the liquid. A similar reaction was run at a higher heating rate (50°C./min); the relative intensity of all the mass peaks were reversed. Most of the sample was sublimed during the initial period with the remaining smaller sample again melting and vaporizing at the higher temperature.

-44-
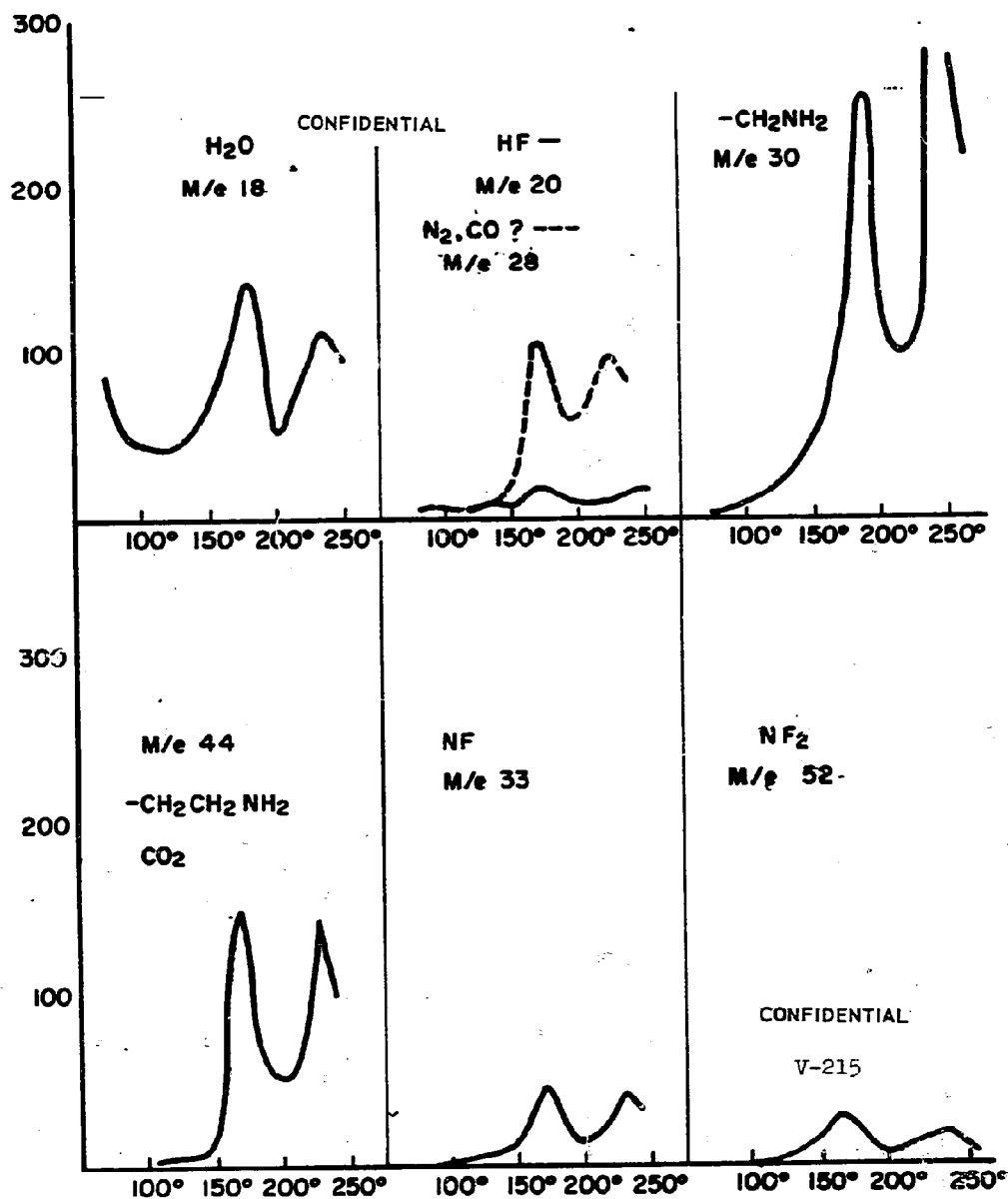
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(U)   Fig. 19 - MTA Results on Recrystallized INFO-635P
at a Heating Rate of 3°C./min.

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Table XVI

(U) High Resolution Mass Spectra of INFO-635P

M/e	Species	Relative Amounts at Various Temperatures, °C.		
		120	140	160
18	H_2O^+	52	14	---
	NH^+	77	20	15
20	HF^+	88	76	13
28	N_2^+	32	34	41
	CO^+	27	39	28
	CH_2N^+	59	49	41
	$C_2H_4^+$	10	11	16
30	CH_4N^+	350	290	200
33	NF^+	35	73	85
42	$C_2H_4N^+$	58	64	103
44	CO_2^+	44	165	182
	$C_2H_6N^+$	200	170	230
52	NF_2^+	32	150	210
66	$N_2F_2^+$	---	---	Some
67	$Cl^{35}O_2^+$	---	---	130
69	$Cl^{37}O_2^+$	---	---	49
	$C_3H_3ON^+$	---	---	Low
75	$C_2H_2NCl^{35+}$	---	---	37
80	$CONF_2^+$	---	---	10
87	$C_3H_5O_2N^+$	---	---	53
123	$C_6H_4N_2F^+$	---	---	16
132	$(NF_2)_2CO^+$	---	---	0
156	$C_3H_6ON_3F_3^+$	---	---	Some
168	$C(NF_2)^+$	---	---	Some
184	$(NF_2)_3CO^+$	---	---	0

7. Decomposition Mechanism (U)

(U) Thermal evaporation depends primarily on the transfer of kinetic energy for evaporation. This evaporation occurs from an adsorbed layer, and for equilibrium between vapor and condensate to be established and maintained the probability of evaporation must follow a cosine distribution (26), i.e., the molecules condense and re-evaporate. The most sophisticated treatments of the stepwise process of the evaporation rate of crystals can be found in the literature (27,28). The cases described usually deal with the evaporation of crystals for which the only participating species is monomeric. If the evaporation of a material involves monomeric and dimeric species, nine sets of reaction rates are necessary for which there is no general analysis of the kinetics. If evaporation of a compound leads to elemental or disproportionated vapor, the multiplicity of reaction rates necessary to describe the system also leads to further complexity.

(C) A mechanism supported by the data is proposed. The initial step is a proton transfer with the subsequent formation of the free amine, $(NF_2)_3COCH_2CH_2NH_2$, and perchloric acid, both adsorbed on the surface of the unreacted solid. The next sequence of reactions depends upon the reaction parameters of pressure and temperature. Under vacuum, the desorption of the free amine and perchloric acid occurs readily. Vapor phase decomposition follows; however, the extent of decomposition is dependent upon the temperature and path length. In a closed system the decomposition is complete, since no N-F compounds are found in the gas phase at long times. In an open system, the vapors pass into a cold zone where the unreacted free amine and perchloric acid condense out as INFO-635P. The remaining gaseous products are composed mainly of SiF_4 (HF), CO_2, N_2F_4, N_2F_2, and N_2O.

(C) Solid phase decomposition is very slow at temperatures less than 180°C. in a vacuum system. The solid reaction may be induced by either increasing the pressure or the temperature of the reaction. The proton transfer step still occurs. The free amine can still be transferred into the vapor phase, but the perchloric acid, which appears to have a lower vapor pressure than the free amine, tends to remain behind. It is believed that this perchlorate increases the rate of reaction. These reactions are shown below:

$$(NF_2)_3COCH_2CH_2\overset{+}{N}H_3\overset{-}{C}lO_4 \underset{r_2}{\overset{r_1}{\rightleftharpoons}} (NF_2)_3COCH_2CH_2NH_{2(ad)} + HClO_{4(ad)} \quad (1)$$

$$(NF_2)_3COCH_2CH_2NH_2(ad) \xrightarrow{r_3} (NF_2)_3COCH_2CH_2NH_2(g) \quad (2)$$

$$\downarrow r_8 \qquad\qquad\qquad\qquad \downarrow r_5$$

Gas, Solid Products   Gas Products

$$HClO_4(ad) \xrightarrow{r_4} HClO_4(g) \quad (3)$$

$$\swarrow r_9 \qquad\qquad\qquad \searrow r_6$$

Gas, Solid Products   Gas Products

$$HClO_4(g) + (NF_2)_3COCH_2CH_2NH_2(g) \xrightarrow{r_7} (NF_2)_3COCH_2CH_2\overset{+}{N}H_3\overset{-}{C}lO_4(s) \quad (4)$$
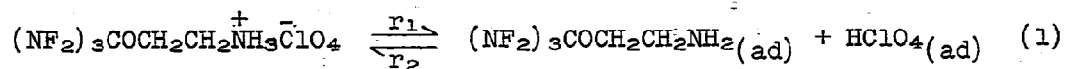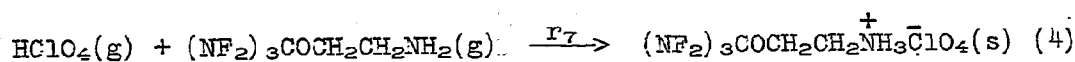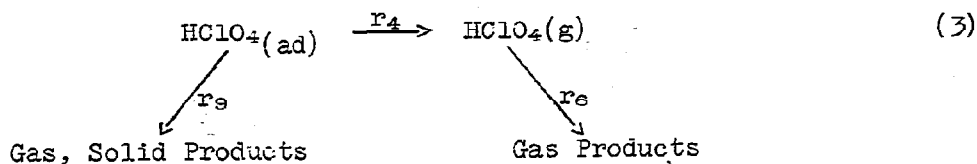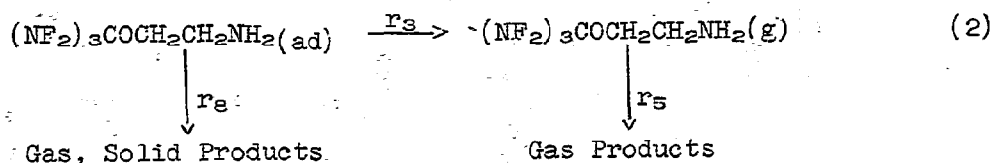
The gaseous and solid products produced complicate the overall mechanism very rapidly. However, the relative rates may be ordered into a general outline. The initial conditions are a vacuum and a temperature of 170°C. Then: $r_2 \ll r_1 > r_4$; r_5, r_6, r_7 are a function of the experimental parameters, but generally $r_7 > r_5$, r_6; $r_8 \ll r_3$; and $r_9 \ll r_4$. If the reaction conditions are changed to increase the overall reaction rate, then the relative rates have changed; the most probable and important change being $r_9 > r_4$.

B. POLY FA-BDE (U)

1. Hot Stage Microscopy (U)

(U) When prepared by the "foaming" procedure recommended by Esso, poly FA-BDE appeared similar to INFO-635P under the microscope. No visible changes were noted in the irregularly shaped particles when heated under continuous vacuum until about 240°C. where melting began and decomposition was indicated by bubble formation. At 245°C. only a pale yellow liquid remained in the observation dish. When the heating was continued, a brittle amber film was formed. At room temperature this film was found to be insoluble in all solvents tried, suggesting that the decomposition yielded a highly crosslinked polymer.

2. Thermogravimetric Analysis (TGA) (U)

(U) A TGA experiment run under continuous vacuum at a heating rate of 2°C./min. indicated that the rate of weight loss was greatest beginning at 190°C., although the rate was already substantial at about 160°C. At approximately 220°C. the rate slowed markedly. The overall weight loss curve then leveled at about 95 percent near 500°C. where the heating was discontinued. Although not analyzed, the residue appeared to have been reduced to carbon only.

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(U) An apparent activation energy of 46 kilocalories for on-set of thermal decomposition was obtained from a set of TGA ex-periments. To obtain this value, experiments were run under a continuous vacuum which removed the decomposition gases as they were formed, minimizing the secondary reactions. From the rates of weight loss taken early in decompositions at 155°, 160°, 165°, 170°, and 180°C., the Arrhenius plot shown in Figure 20 was con-structed. When an activation energy is calculated in this manner, no particular reaction order is implied, but the energy so ob-tained should approximate that necessary for the onset of degrada-tion.

3. Mass Spectroscopy (U)

(U) The experiments which were made using the sensitive method of mass thermal analysis (MTA) indicated that break-up of the polymer occurred at least as early as 130°C. and that the degrada-tion consisted of two major phases. The first phase had its max-imum rate at about 220°C., corresponding to the melting observed in the hot stage microscopy. The first phase left an amber residue which then slowly decomposed at higher temperatures. The MTA experimental work considered only the first phase.

(C) Figure 21 shows the type of data obtained by method of MTA. The experiments on poly FA-BDE at different heating rates indicated that during the early decomposition the peaks of great-est intensity in every case were those due to NF^+ and NF_2^+. Plots similar to those in Figure 21 were made for the other important peaks in the mass spectra. In these spectra, the largest peaks observed were at M/e 20, 28, 33, 47, 52, 61, 66, 80. Peaks of lower intensity were 42, 43, 53, 71 and 85. Larger fragments were observed in many spectra, but these occurred after the decom-position was beyond the very early stage. The most frequently occurring of the larger fragments were M/e 117, 132, 136, 149, 153 and 155.

(C) Using the high resolution mass spectrometer and working at 135°C., most of the intense peaks in the MTA spectra were iden-tified. They are shown in Table XVII together with their approx-imate relative amounts at 135°C. Although M/e 53 was not measured, the assignment of HNF_2 to this mass is reasonable when it is con-sidered that mass 34, which is in the cracking pattern of HNF_2, is present in the right amount in the MTA spectra. NF_3^+ was assigned to M/e 71 since NF_3 does have a sizeable parent peak and was found to be one of the major gaseous products in the slow thermal decompositions to be described. $N_2F_3^+$ was assigned to M/e 85 as a mass cracking fragment from N_2F_4 which is also a known gaseous product of the early phase of degradation. Mass 85 cannot be attributed to SiF_3^+ since the high resolution decompositions were performed in a stainless steel capillary.

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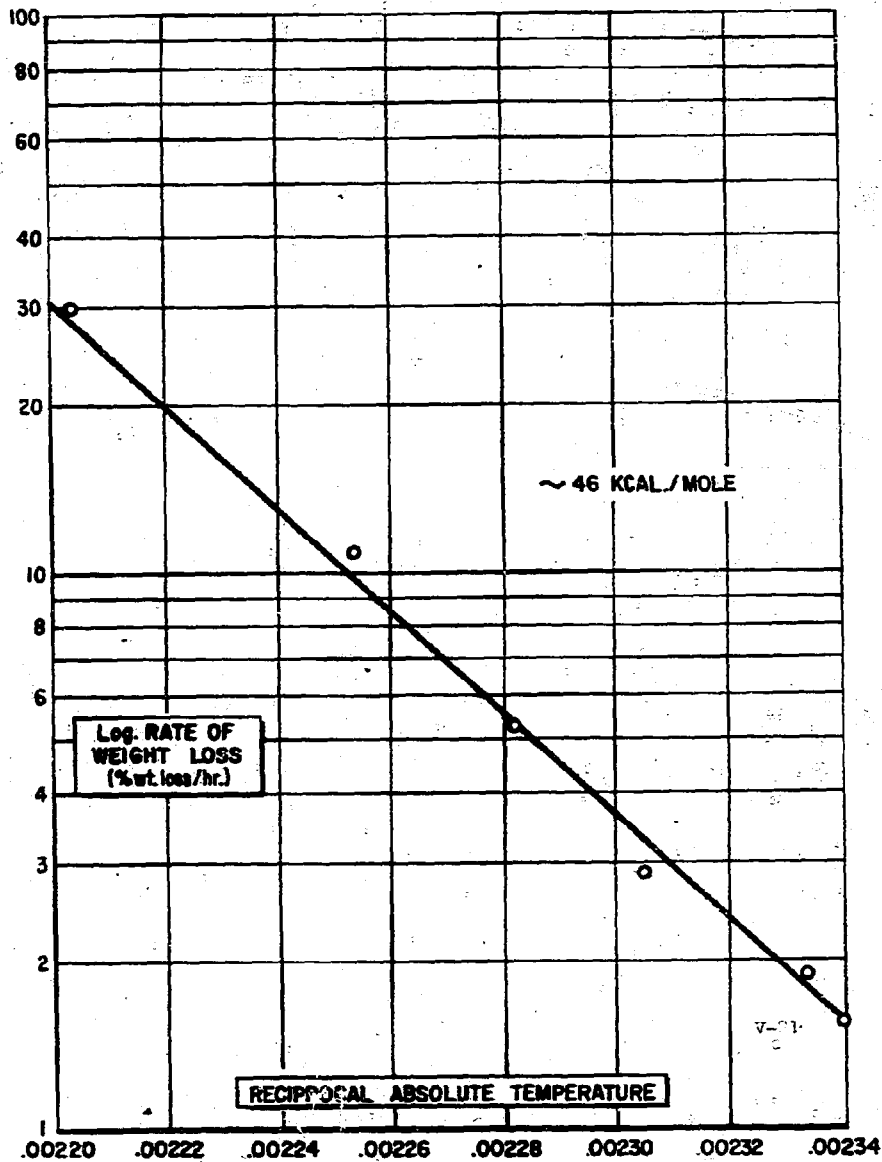
(U) Fig. 20 - "Activation Energy" from TGA Data
on Poly FA-BDE

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PEAK HEIGHTS
(ARBITRARY SCALE)

MTA EXPERIMENT
DISCONTINUED AT
260°C LEAVING
AMBER RESIDUE

NF

NF$_2$

V-217

TEMPERATURE, °C

100   140   180   220   260   300   340

(U)   Fig. 21 - Illustrative Data from MTA Experiment
          at a Heat Rate of 2°C./min.

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Table XVII

(U) Fragment Identification from Poly FA-BDE Using High
Resolution Consolidated 110 Mass Spectrometer at 135°C.

M/e	Assignment	Approx. Rel. Amt.
20	HF^+	--
33	NF^+	200
52	NF_2^+	~300
61	$CONF^+$	38
66	COF_2^+	20
80	$CONF_2^+$	50
28	N_2^+	100
	CO^+	.14
47	COF^+	200
	N_2F^+	50
42	$C_2H_2O^+$	12
	NCO^+	2
43	$C_2H_3O^+$	10
	$HNCO^+$	2
44	CO_2^+	25

Also: M/e 53, 71, 85 (not measured)
Attributed to: HNF_2^+, NF_3^+, $N_2F_3^+$

(C) The appearance of M/e 28 (mainly N_2 but with some CO),
concomitant with NF and NF_2 and in the amount indicated by the
high resolution and MTA spectra, means that secondary decomposition
reactions had already taken place in the matrix of the polymer
sample. Further, since the ions N_2F^+ and $N_2F_3^+$ were seen, it
implies that N_2F_4 was made prior to the electron beam. This can
be concluded because in the mass spectral cracking patterns of
known NF compounds N_2F^+ and $N_2F_3^+$ only appeared from compounds
which already contained the nitrogen-nitrogen bond.

(C) Therefore, in spite of the high vacuum conditions which
were obtained in the mass spectroscopic work, and the positioning
of the tiny samples within a few millimeters of the ionizing beam,
secondary reactions still occurred. Thus, it does not appear pos-
sible to single out with absolute assurance the first thermal frag-
ment by the MTA method as it was performed. On the other hand, a
reasonable argument can be made for the postulation that large
quantities of NF_2 are formed as an initial step in the decomposition
of poly FA-BDE.

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(C) The relative preponderance of M/e 52 and 33 in all mass spectra and the absence of large fragments in the early stage of decomposition implies that NF_2 comes directly from the polymer and not from the mass cracking of larger fragments. Apparently, a large portion of the difluoroamino radicals formed proceed directly into the ionizing beam and appear as NF_2^+ and NF^+. Other $\cdot NF_2$ radicals formed in the polymer matrix undergo recombination and secondary reactions, yielding compounds such as N_2F_4, N_2, CO, HNF_2, and HF.

(C) In the slow thermal decompositions to be described later, it was found that another early gaseous product was N_2F_2. If this compound were to get into the ionizing beam without undergoing reaction or decomposition to fluorine and nitrogen it would appear in the mass spectra as NF^+. Therefore, some of the M/e 33 appearing in the MTA spectra comes from this source in addition to the mass cracking of $\cdot NF_2$.

(C) The NF_2^+ and NF^+ in the mass spectra cannot be explained by mass cracking of N_2F_4 only. Nor can the N_2^+ be explained in this manner. For the amounts of NF_2 and NF observed, the parent peak, $N_2F_4^+$, would easily have been observed, but was not. Similarly, if the N_2^+ observed came from N_2F_4, then $N_2F_4^+$ (M/e 104) should again have shown up strongly. Therefore, it would appear that nitrogen came from secondary reactions and NF_2^+ and NF^+ mainly from ionization and cracking of difluoroamino free radicals.

(C) The MTA work also gave an indication of the order in which early products appeared as judged by their spectral intensity. On this basis, HF seemed to be formed slightly before HNF_2 and COF_2, and NF_3 and CO_2 appeared to follow all three of these. This interpretation is not conclusive since an unmeasured factor is that of the relative sensitivity of the spectrometer towards these particular masses and the dynamic nature of samples undergoing decomposition. The more important conclusion is that these compounds were identified as gaseous products of the early stage of decomposition.

(C) Although CO_2 (M/e 44) was observed almost immediately in the MTA experiments, its peak height remained low relative to others in the spectrum until the decomposition was well advanced and the relative amounts of NF_2 and NF decreased substantially. At this time, CO_2 made a substantial contribution to the total ion current.

(C) Throughout the degradation of poly FA-BDE in the MTA method, small amounts of $C_2H_3O^+$ and $C_2H_2O^+$ appeared. These are attributed to fragmentation of the epoxy polymer end groups.

(C) No high resolution identification of the large fragments was possible. However, M/e 132, which also appears in the mass cracking pattern of BTU, could be postulated as $(NF_2)_2CO^+$. The occurrence of this would explain the presence of the measured fragment, $CONF_2^+$ and $CONF^+$ as well as some of the CO^+.

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4. Slow Thermal Decomposition Experiments (U)

(U) The gaseous products from decompositions made in the temperature range 160°-180°C. showed that the degradation of poly FA-BDE is a complex phenomenon. The studies made under vacuum, low pressure of gaseous products, and cumulative pressure of gaseous products demonstrated the extensiveness of reaction between early gas products and the solid substrate.

(C) When the decomposition gases were allowed to accumulate and their total pressure recorded as a function of time, sigmoid-type curves, shown in Figure 22, were obtained. Decompositions made in this manner produced weight losses of 70-75 percent if terminated when the decomposition curve reached its plateau. The residues from these experiments were amber, insoluble in common organic solvents, and had the fairly consistent composition shown in Table XVIII. Infrared examination of these residues indicated a structure very similar to carbon-fluorine polymers. By infrared analysis the hydrogen remaining was found to be bonded to carbon and the oxygen was present as ether and carbonyl linkages. The "final" gas products were identified as HF, N_2, NF_3, CO_2, compounds of the type $C_xH_yF_z$ (chiefly CF_4), and small amounts of N_2O and COF_2. A completely satisfactory mass balance was not obtained because of the difficulty in determining the exact amount of HF formed. The best final gas product analysis is shown in Table XIX.

Table XVIII

(U) Elemental Analysis on Decomposition Residue

Element	Percent Composition	Percent of Sample Lost to Vapor
C	31.6 ± 0.2	44.8
H	2.28 ± 0.25	50
N	10.17 ± 0.11	84.7
F	38.1 ± 0.2	79.0
O	17.8	53.3

(c) The low pressure and vacuum decomposition experiments showed that the early gas products were N_2, N_2F_2, N_2F_4, HF, HNF_2, NO, NF_3, CO, and COF_2. Of these, only N_2, NF_3 and HF were found in the "final" gas products to any significant extent. Thus, the others can be considered "stable intermediates" and are converted to the final products via secondary reactions with the solid substrate (or other gases).

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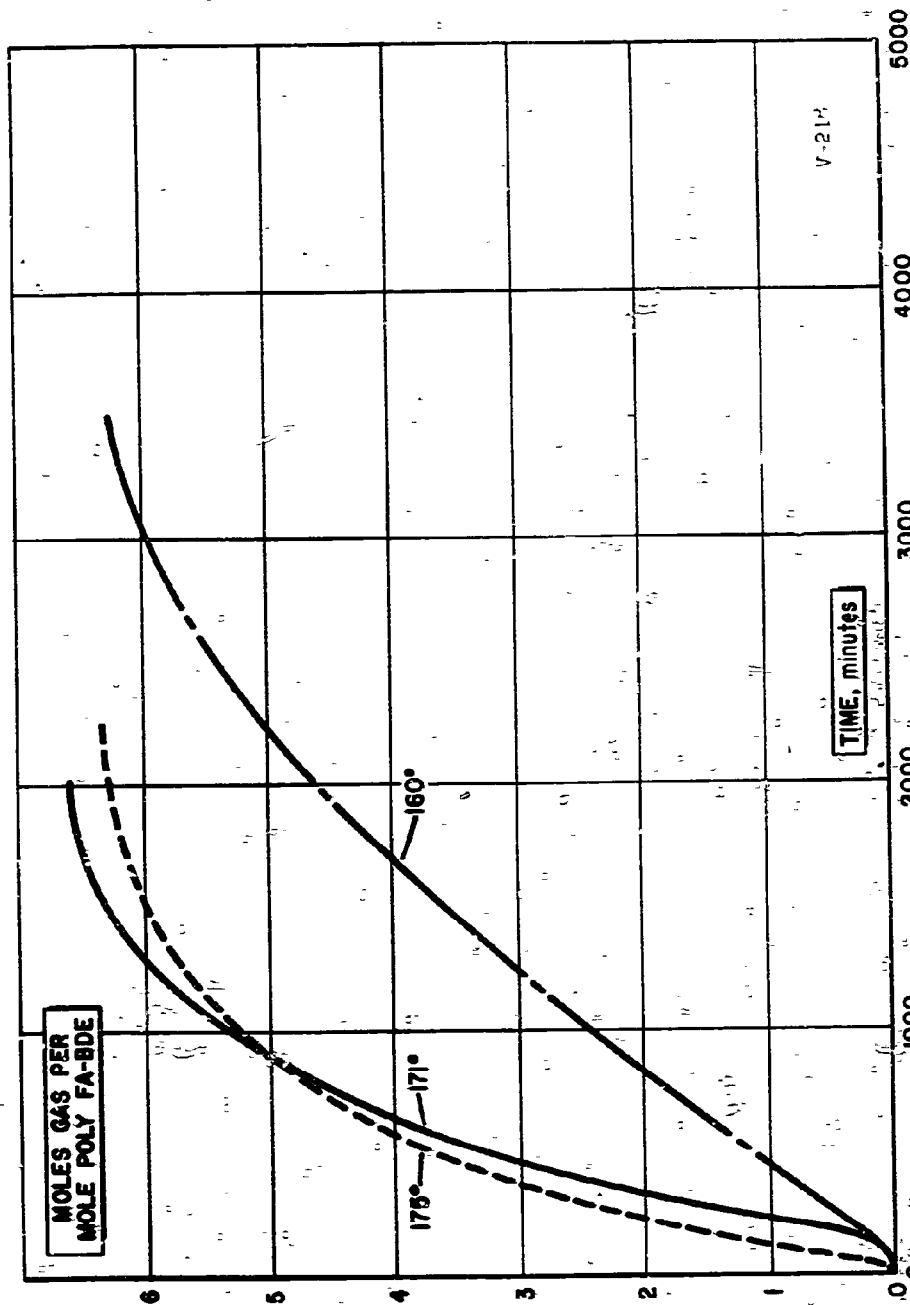
(U) Fig. 22 - Slow Thermal Decomposition of Poly FA-BDE In Monel Reactor

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Table XIX

(C) Final Gas Products at 175°C.

Compound	Percentage
N_2	30.1
N_2O	0.8
CO_2	15.85
CF_4	3.75
NF_3	14.90
HF	34.6

(C)   Extensive formation of nitrogen was observed even from a gas sample taken 15 minutes after immersion of the monel reactor into the heating bath. Thus, the degradation was already at an advanced stage in at least a portion of the poly FA-BDE.

(C)   The extensiveness of secondary reactions in decompositions of poly FA-BDE was demonstrated in an experiment in which samples were decomposed for increasing intervals at 175°C. while a continous vacuum was applied. After 24 hours, a weight loss of only 26 percent was incurred as compared to about 70 percent when the gases were allowed to accumulate and react with the solid. Furthermore, the elemental analysis on the residue, shown in Table XX, was considerably different from that reported earlier. These results show that under the continuous vacuum conditions secondary reactions were substantially reduced, and that most of the weight loss probably came from the group $-O-C(NF_2)_3$.

Table XX

(C) Residue Analysis from Vacuum Decomposition

Element	Percent in Residue	Percent of Orig. Sample Lost to Vapor State
C	19.95	10
H	>1.7	<8
N	17.0	34.5
F	48.5	31.2
O	12.7 (Diff.)	13.1

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(C)   It was found that the foregoing residue consisted of Freon-soluble and -insoluble portions and NMR and infrared analyses of the soluble portion indicated that it was mainly undecomposed poly FA-BDE. However, the insoluble fraction was still slightly shock sensitive and slightly active to KI solution which suggested a partially decomposed state. Table XXI shows the results of elemental analyses on the Freon-soluble and -insoluble fractions together with that calculated for the original poly FA-BDE. Included in the data is the "active fluorine" analysis for all three materials as determined by the titration of iodine liberated from sodium iodide in acetone solution. These data provide further justification for the assumption that the Freon-soluble fraction is proportional to the undecomposed poly FA-BDE.

Table XXI

(U)   Analytical Data on Freon 113-Soluble and -Insoluble .
Fractions from Poly FA-BDE Decomposition

Element	Original Poly FA-BDE	Freon-Soluble Fraction	Freon-Insoluble Fraction
Carbon	16.4 calc.	16.8	20.5
Hydrogen	1.35 calc.	1.4	1.72
Nitrogen	19.2 calc.	20.4	16.4
Fluorine (total)	52.1 calc.	50.9	43.9
Active fluorine[a]	38.0	36.1	25.8

[a]By titration of iodine liberated from sodium iodide in acetone solution.

(U)   On this basis, experiments were carried out at four different temperatures. At each temperature, samples of partially decomposed poly FA-BDE were removed at intervals from the constant temperature bath and the Freon-soluble portion separated. The results of these experiments are plotted in Figure 23 as percent of original sample weight that was Freon-soluble at the indicated time intervals. As in the case of the pressure-time data mentioned earlier, these data did not follow a first order plot and attempts to fit the data to an equation failed. Initial decomposition rates were applied to an Arrhenius plot to obtain a value for the activation energy. The result, 46.9 kilocalories, shown in Figure 24 is in fair agreement with the value obtained by the method of TGA described earlier.

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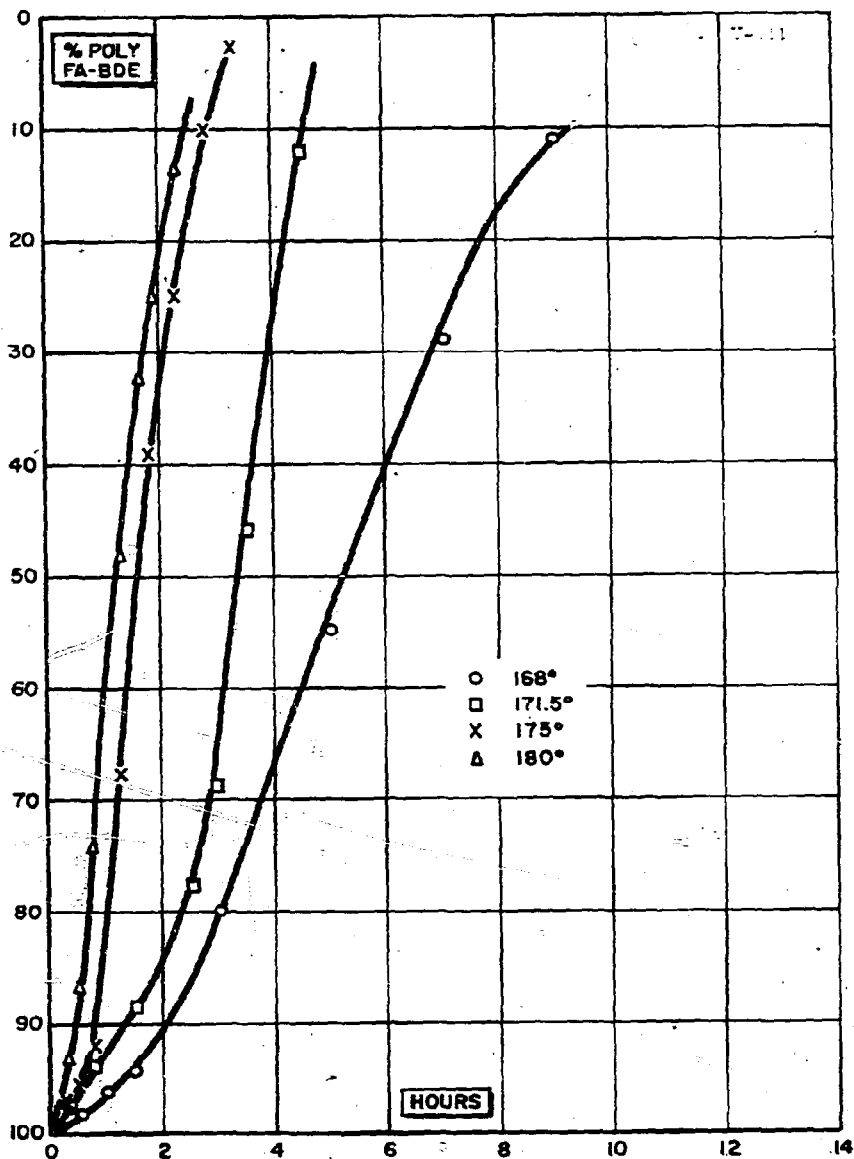
(U) Fig. 23 - Disappearance of Poly FA-BDE as Measured
by Freon 113 Solubility of the Residues.

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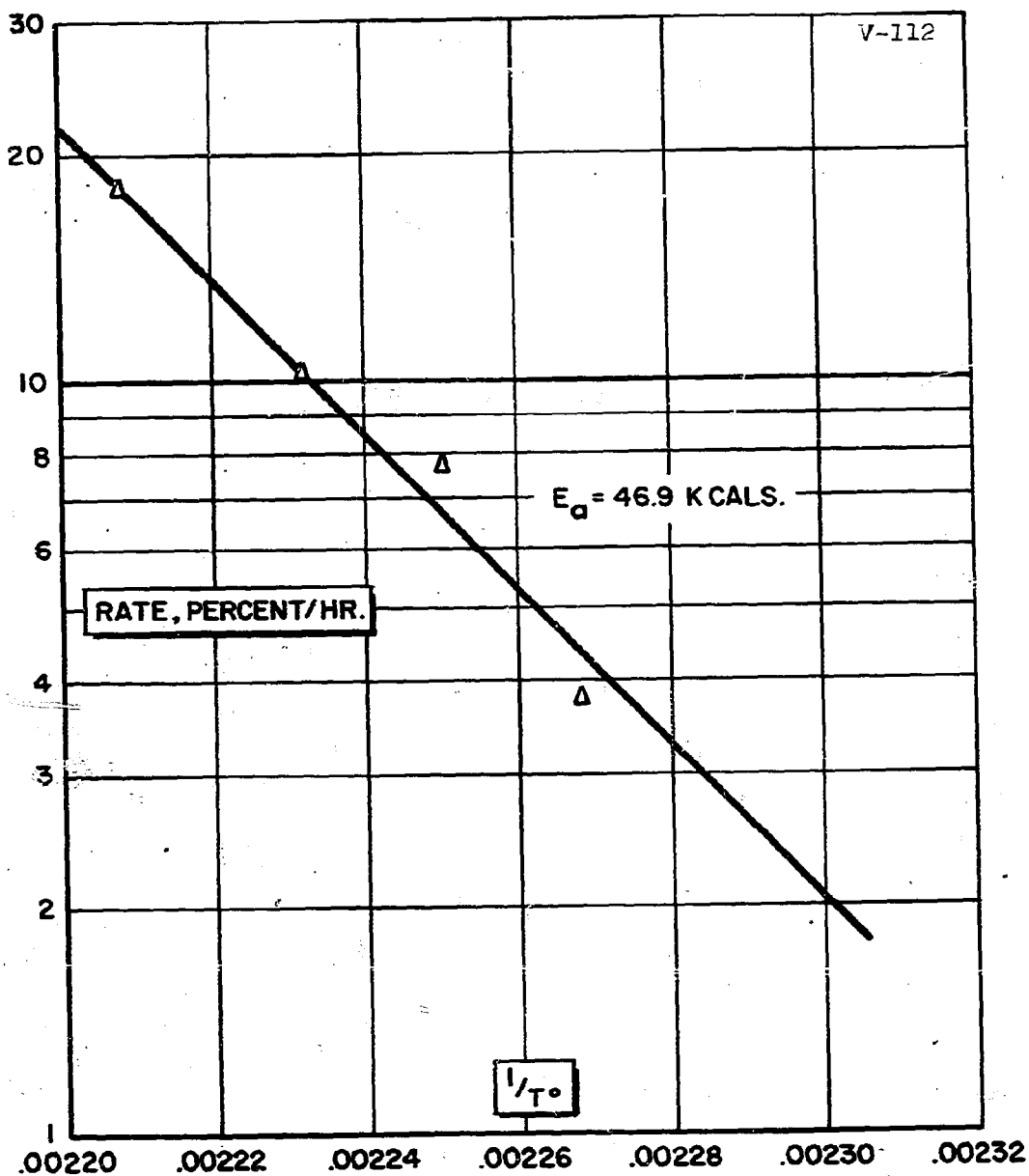
(U) Fig. 24 - Arrhenius Plot; Rate of Disappearance
of Poly FA-BDE

(U) Apparent activation energies were also obtained from the decomposition performed in such a manner that the pressure of decomposition products did not exceed about 6 millimeters. This was done by pumping the reactor to zero pressure after sampling for VPC analysis and then allowing the pressure to build up again to a few millimeters. The process was repeated several times during the early stages of decomposition at several experimental temperatures. From the known experimental parameters, the rates of decomposition were expressed in terms of millimoles of gas evolved. A series of average rates, r_1, r_2, $\cdots r_n$ were thus obtained at corresponding average times, t_1, t_2, $\cdots t_n$, from which the rate of gas evolution, r_o, at $t=o$ was determined by extrapolation. In this manner, a value of r_o was obtained for each experimental temperature. From the slope of an Arrhenius plot of log r_o versus $1/T$, an activation energy of 44.4 kilocalories was calculated for onset of decomposition (Figure 25).

(C) During the course of the above experimental work, each sample taken was analyzed by vapor phase chromatography over a column packed with 30% siloxane on Chromosorb W at $0°C$. For the last experiment in this series, a portable mass spectrometer was attached to the VPC exit tube to identify and to determine the order of elution of the various decomposition gases. The spectrometer was used on all five of the samples taken during the course of this experiment. Examination of the mass spectral data revealed that most of the VPC peaks were not "pure". With the possible exception of HNF_2, the peaks were composed of at least two, and sometimes, three or four components. This made construction of concentration plots of individual gaseous components impossible from the sets of data. That portion of gas samples taken for VPC analysis which was non-condensable in a liquid nitrogen trap was the most abundant fraction as judged by its relative peak height. These non-condensable portions consisted of nitrogen and undetermined amounts of CO. Assuming peak heights as an approximate quantitative measure, this fraction represented almost half the total gas pressure throughout most of the thermal decomposition studied. If the average rate of non-condensable gas formation is calculated from the experimental data and use made of the peak heights obtained in the VPC analyses, a rate of N_2+CO formation at zero time can be extrapolated for each temperature. This was done for four temperatures for which the data were complete. The values of r_o so obtained are shown on an Arrhenius plot in Figure 26. Considering the assumption necessary to make this plot, the apparent activation energy of 49.4 kilocalories calculated in this was of the same magnitude as that found by using the rates of total gas evolution.

C. bis[tris(DIFLUOROAMINO)METHYL]UREA, BTU (C)

(U) The experimental work on BTU during the year was limited to the preparation of pure samples to perform MTA, hot stage microscopy and exploratory thermal decompositions.
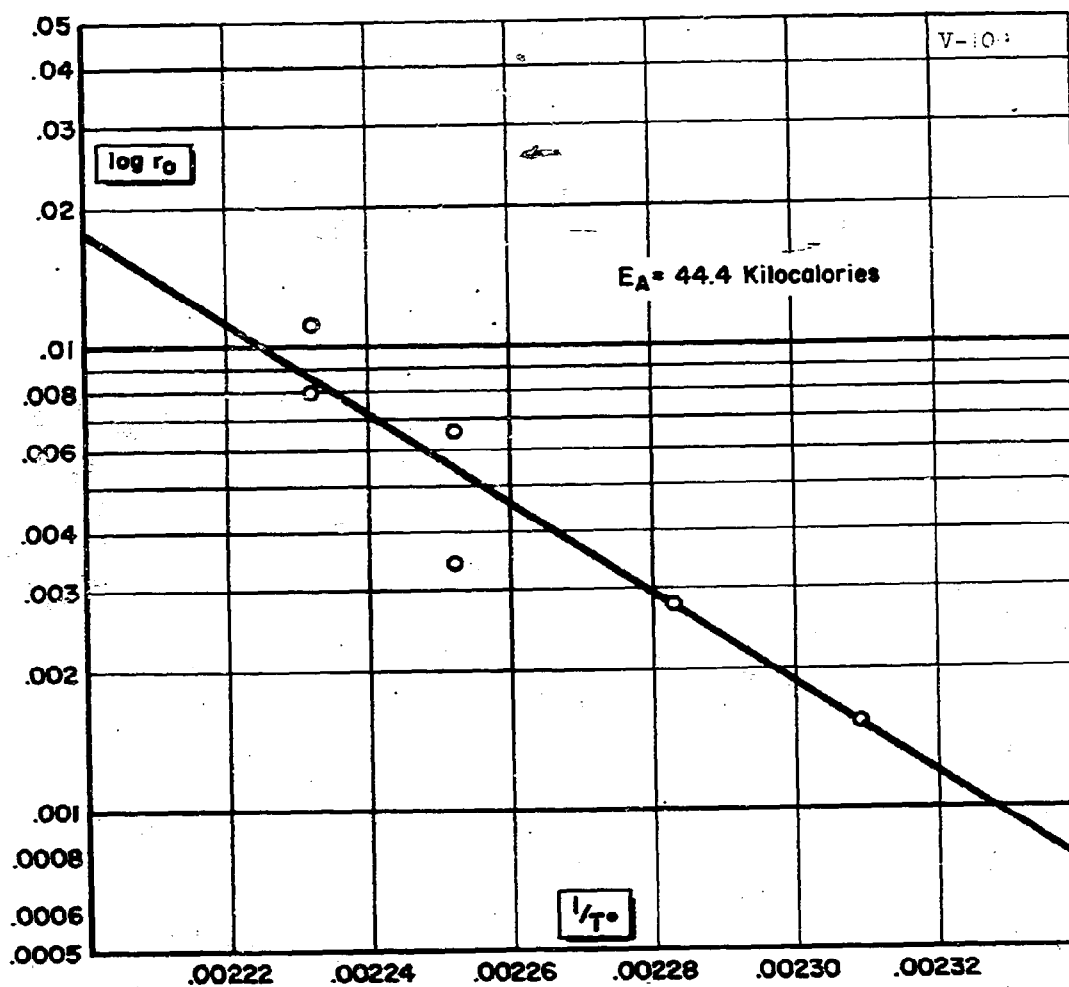
(U) Fig. 25 - Arrhenius Plot; Total Gas Evolution Rate at Zero
     Time; Millimoles per Minute per 200 Mg. Poly FA-BDE

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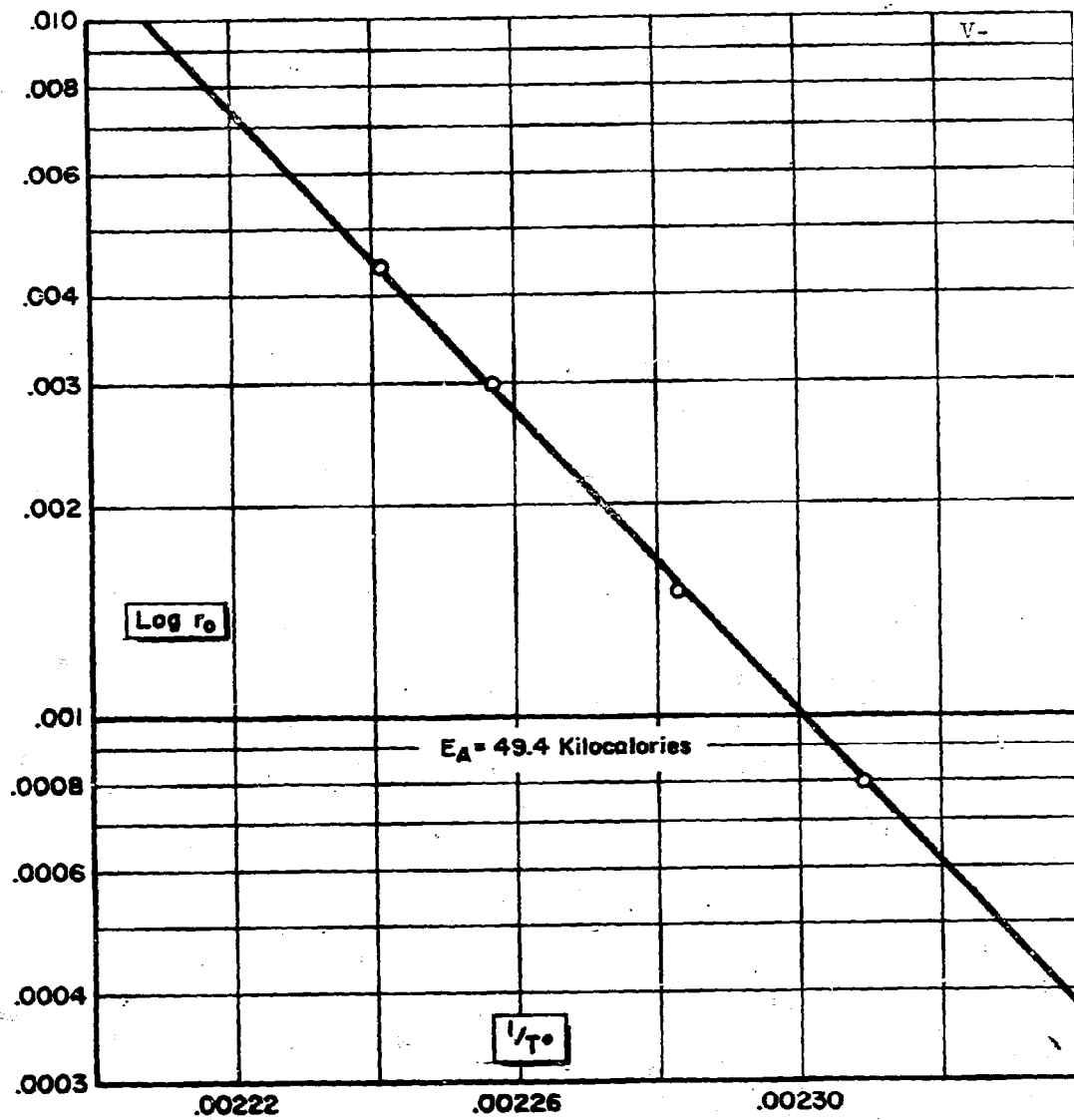
(U) Fig. 26 - Arrhenius Plot; $N_2(+CO)$ Rate at Zero Time;
        Millimoles Gas per Minute per 200 Mg. Poly FA-BDE

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(U) To insure that the BTU was free of the halocarbon wax in which it was received, it was found necessary to sublime the crystals obtained by the recrystallization procedure set forth by American Cyanamid Company. Neutron activation analysis for chlorine on BTU recovered by the recrystallization procedure indicated the presence of chlorine even in samples crystallized a second time. If the recrystallized solid was sublimed, however. the chlorine content was either barely detectable by this method. or absent.

(U) In the hot stage work it was found that, when BTU crystals were heated while exposed to the atmosphere, considerable melting with decomposition due to reaction with the atmosphere occurred as low as 80°C., leaving an amber residue. On the other hand, when BTU was heated under continuous vacuum, it merely sublimed away, and crystallized again on cooler portions of the unit.

(C) As was anticipated, the MTA method proved of limited value with BTU because of its tendency to sublime. Even at 40°C., sublimation was substantial enough to obtain a spectral pattern for BTU. Of the four runs made, the cracking pattern obtained on sublimed material at a heating rate of about 3°C. per minute is shown in Table XXII. These data should be considered tentative because of the possibility that some decomposition might have occurred with mass fragments from such break-up of BTU being superimposed on the BTU, mass cracking pattern. The possibility that this did occur was increased by an apparent water absorption by the sample during handling. This was indicated by sizable peaks at 17 and 18. In order to be certain of a pure BTU pattern, the loading of the spectrometer would have to be done in absence of the atmosphere. In the type of work reported here, a short exposure to the atmosphere was unavoidable. Accepting the data in Table I with the above reservation, the small fragments in the spectrum can be derived from the three largest when these are formulated as follows:

$$M/e = 132 \qquad M/e = 158 \qquad M/e = 168$$

$$\underset{NF_2 \quad NF_2}{\overset{\overset{\displaystyle O}{\overset{\|}{C}}}{\diagup \hspace{0.5em} \diagdown}} \qquad \underset{}{\overset{\overset{\displaystyle O}{\overset{\|}{-C-N=C}}}{\diagup^{NF_2} \diagdown_{NF_2}}} \qquad \overset{NF_2}{\underset{NF_2}{-C-NF_2}}$$
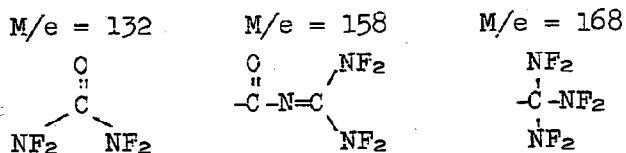
(C) The thermal decomposition of pure BTU takes place in the vapor state after sublimation. This was shown by suddenly inserting a 3 mg. sample into a chamber at 130°C. A water-cooled condenser directly above the hot zone condensed the BTU vapor immediately. No decomposition gases were detected, and the BTU completely recovered. In preliminary experiments, 100 mg. samples were decomposed at 100°C. and 130°C. in the monel systems. Infrared analyses of the gaseous products indicated the presence of HF (as SiF_4), CF_4, NF_3 and Tris-I. No further work on this compound is planned at the present time.

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Table XXII

(U) Mass Spectral Pattern Obtained on Subliming
BTU at 52°-57°C.

M/e	Relative Pattern	M/e	Relative Pattern	M/e	Relative Pattern
12	16	43	34	70	4
13	4	44	15	71	4
14	11	45	24	73	7.5
15	3	46	58	74	4
16	9	47	35	78	11
19	6.5	50	14	79	13
20	32	51	19	80	9
26	27	52	70	81	1
27	17	53	2	83	4
28	15	54	48	87	4
29	37	55	4	88	37
30	7.5	57	2	92	3
31	100.0	59	56	97	2
33	70	60	18	98	10
34	4	61	56	107	18
38	2	62	1	108	4.5
39	3	64	30	113	9
40	34	66	3	132	61
41	39	68	20	158	9
42	30	69	35	168	9

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SECTION V.

(U) CONCLUSIONS

A. INFO-635P (U)

(C) The thermal decomposition of INFO-635P is initiated in the solid phase by a proton transfer forming the adsorbed free amine and perchloric acid. Subsequent reaction steps are dependent on the evironment of the solid.

(C) Slow heating in vacuo results in sublimation. The decomposition continues in the vapor phase until a minimum pressure is reached at which point the major portion, if not all of the decomposition, reverts back into the condensed phase. The initial gaseous products from these reactions certainly suggest an endothermic process involving C-NF$_2$ bond rupture as an early reaction.

(C) Rapid heating or decomposition under pressure results primarily in a solid phase reaction of perchloric acid with the remaining solid. The lack of NF$_2$ compounds in the gas phase indicates a very rapid and highly exothermic process.

(U) The chemical kinetics of the decomposition are believed to be less important to the problem of sensitivity than the physico-chemical process of proton transfer and desorption. Once nucleation has occurred the reaction proceeds to completion, or until the heating is discontinued.

(C) INFO-635P may possibly be less sensitive if the proton transfer step in the mechanism could be controlled. This may be accomplished in one of two ways: (1) by supplying excess protons to reverse the equilibrium step, or (2) by eliminating the proton. In the first case the addition of anhydrous perchloric acid, or the synthesis of the bisulfate salt of the amine or of a double salt, may prove successful. The second method appears to be more promising because eliminating the proton would most likely solve the problem of sublimation. The synthesis of the quarternary salt of INFO, (NF$_2$)$_3$COCH$_2$CH$_2$N(CH$_3$)$_3$ClO$_4$, may prove to be most effective in decreasing the sensitivity.

B. POLY FA-BDE (U)

(U) The experimental data obtained during the course of the experimental program indicated that a complex reaction sequence must prevail when poly FA-BDE is decomposed. Therefore, the research effort was concentrated on defining the initial step and the early stages of the degradation process.

(C) There is good evidence that the initial step is the cleavage of one of the carbon-nitrogen bonds of the tris-difluoramino group and the formation of a difluoramino free radical. The experimental support for this step is as follows:

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(i) In the method of MTA in which high vacuum and milli-gram-size samples were used , the first mass peaks of any mea-surable significance were those at 33 and 52. High resolution mass spectroscopy positively measured these as NF^+ and NF_2^+.

(ii) Under the conditions of mass spectroscopy where secondary reactions were at a minimum, the predominant peaks in the mass spectra were those due to NF_2^+ and NF^+. It is very doubtful that NF_2^+ arose to any significant extent from the mass cracking of larger fragments containing the difluoramino group, since these fragments were not observed in the early stages of decomposition.

(iii) The slow thermal decomposition studies in the monel reactor showed that N_2F_4 is an early and important gaseous pro-duct. The known recombination of difluoroamino free radicals explains the production of this compound.

(iv) The activation energies calculated by the independent methods of TGA, gas evolution, and disappearance of poly FA-BDE are consistent with a free radical mechanism begun by the break-ing of a carbon-nitrogen bond.

(v) The data obtained on the residues and decomposition gases during the early stages of decomposition indicated that the weight loss comes from the pendant group $[-CH_2-O-C(NF_2)_3]$, and chiefly from loss of nitrogen and fluorine.

(U) Not one of the foregoing statements by itself is con-vincing evidence that the first step is the cleavage of a carbon-nitrogen bond; however, when considered together, they convinc-ingly support the postulate that this bond rupture must be the first step.

(U) Mechanistic paths are given which explain the experi-mental data and provide early exothermic reactions to account for the sensitivity of poly FA-BDE.

(C) Once the difluoroamino free radical has been formed, the decomposition mechanism must be considered not only from the standpoint of the possible reactions of $\cdot NF_2$, but also from that of the decomposition of the $R\cdot$ radical formed at the same time. Furthermore, a postulated mechanism must account for the large amounts of N_2 and HF found in the "final" products. In addition, to explain the sensitivity of poly FA-BDE, a highly exothermic reaction should be one of the early steps. It would be highly speculative to postulate a mechanism for the entire degradation process. Poly-FA-BDE has not only a complex molecular configura-tion, but it is one that decomposes by a process that begins in the solid phase and that reaches its maximum rate in a molten phase at approximately 220°C. In the molten phase, where greater mobility is attained, many additional reactions are possible and

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probably do occur. However, reasonable reaction paths can be postulated for the early steps in the degradation which explain the experimental findings within the boundaries of known NF chemistry.

(C) Postulated mechanism for early degradative steps:

$$\begin{array}{cc} \text{H} & \text{H} \\ | & | \\ \text{+C-} & \text{C-O+}_n \\ | & | \\ \text{H}_2\text{C} & \text{CH}_2 \\ (\text{NF}_2)_3\text{C-O} & \text{O-C(NF}_2)_3 \end{array} \longrightarrow \dot{\text{C}}\text{H}_2\text{-O-}\dot{\text{C}}(\text{NF}_2)_2 \ + \ \cdot\text{NF}_2 \qquad (1)$$

$$\cdot\text{NF}_2 \ + \ \cdot\text{NF}_2 \ \rightleftharpoons \ \underline{\text{N}_2\text{F}_4} \qquad (2)$$

$$\text{\textasciitilde} \text{CH}_2\text{-O-}\dot{\text{C}}(\text{NF}_2)_2 \ + \ \cdot\text{NF}_2 \ \longrightarrow \ \text{NF}_3 \ + \ \text{CH}_2\text{-O-C}\underset{\text{NF}_2}{\overset{\text{NF}}{<}} \qquad (3)$$

Alternately--

$$\text{\textasciitilde} \text{CH}_2\text{-O-C(NF}_2)_3 \ + \ \cdot\text{NF}_2 \ \longrightarrow \ \underline{\text{NF}_3} \ + \ \text{\textasciitilde} \text{CH}_2\text{-O-}\underset{}{\overset{\dot{\text{N}}\text{F}}{\underset{}{\text{C}}}}(\text{NF}_2)_2 \qquad (4)$$

$$\text{\textasciitilde} \text{CH}_2\text{-O-}\underset{\text{NF}_2}{\overset{\dot{\text{N}}\text{F}}{\underset{}{\text{C}}}}\text{-NF}_2 \ \longrightarrow \ \text{\textasciitilde} \text{CH}_2\text{-O-C}\underset{\text{NF}_2}{\overset{\text{NF}}{<}} \ + \ \cdot\text{NF}_2 \qquad (5)$$

Then...

$$\text{\textasciitilde} \text{CH}_2\text{-O-C}\underset{\underset{\overset{|}{\text{F}}}{\text{N-F}}}{\overset{\text{NF}}{<}} \ \longrightarrow \ \text{\textasciitilde} \text{CH}_2\text{-O-C}\underset{\text{F}}{\overset{\text{NF}}{<}} \ + \ :\text{NF} \qquad (6)$$

$$:\text{NF} \ + \ :\text{NF} \ \longrightarrow \ \underline{\text{N}_2\text{F}_2} \qquad (7)$$

$$\text{N}_2\text{F}_2 \ \longrightarrow \ \text{N}_2\text{F}\cdot \ + \ \text{F}\cdot \qquad (8)$$

$$N_2F\cdot \ + \ RH \ \longrightarrow \ \underline{\underline{HF}} \ + \ \underline{\underline{N_2}} \ + \ R\cdot \qquad\qquad (9)$$

$$F\cdot \ + \ R\cdot \ \longrightarrow \ \underline{\underline{RF}} \qquad\qquad (10)$$
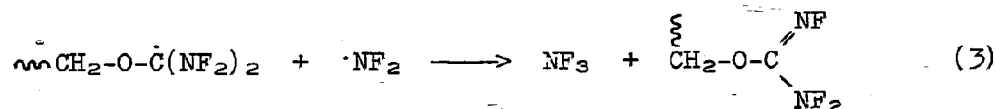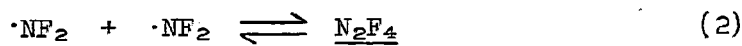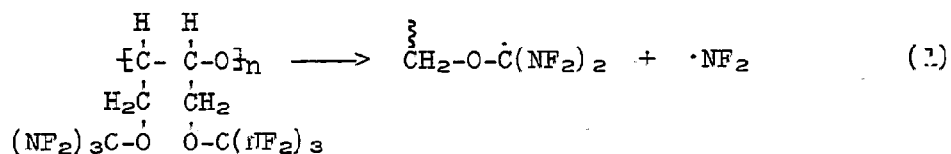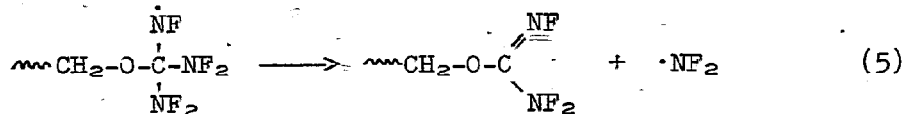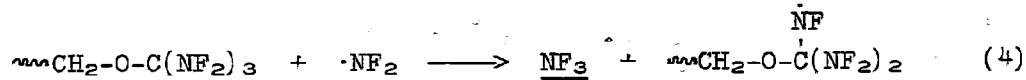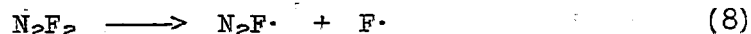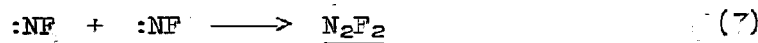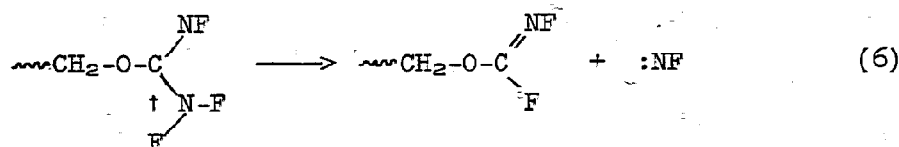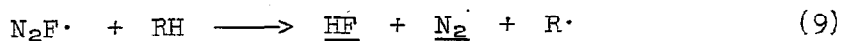
Also, for the observed difluoroamine,

$$RH \ + \ \cdot NF_2 \ \longrightarrow \ R\cdot \ + \ \underline{\underline{HNF_2}} \qquad\qquad (11)$$
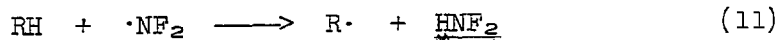
(C) In addition, when a difluoroamino free radical is not available at the reaction site to participate in Reaction (3),

$$CH_2\!\!-\!\!O\!\!-\!\!C\!\!-\!\!NF_2 \ \longrightarrow \ \cdot CH_2 \ + \ O\!\!=\!\!C\!\!\begin{smallmatrix}NF_2\\ \\ NF_2\end{smallmatrix} \qquad\qquad (12)$$
$$\begin{smallmatrix}|\\ NF_2\end{smallmatrix}$$
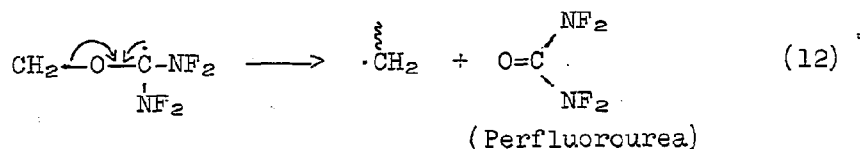
(Perfluorourea)

(C) Once formed, perfluorourea would decompose with great exothermicity, for example, to COF_2, N_2 and F_2:

$$O\!\!=\!\!C\!\!\begin{smallmatrix}NF_2\\ \\ NF_2\end{smallmatrix} \ \longrightarrow \ \underline{\underline{COF_2}} \ + \ N_2 \ + \ F_2 \qquad\qquad (13)$$

(U) Such a path may indeed be possible in the case of a sample suddenly subjected to initiation by a high localized energy source such as impact or spark.

(C) In the foregoing, no consideration has been given to the possibility of reaction between groups on adjacent polymer chains. The possibility of this occurring during slow thermal decomposition is suggested by the formation of a residue which appears to be a highly crosslinked polymer. Where sterically permitted, such inter-chain reactions are quite possible through formation of intermediate ring system. The result would be the production of HF and/or NF_3 and the consequent formation of a nitrogen-containing bridge from a carbon atom of one polymer chain to a carbon atom on an adjacent chain. The elimination of HF in the process of forming such a bridge should also result in substan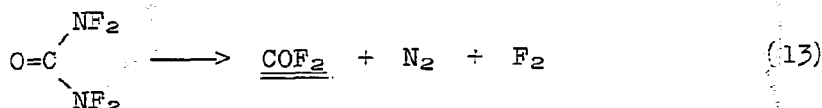tial exothermicity. Although bridge-forming reactions might be important in determining the products obtained in slow thermal decomposition, they are probably of little consequence in determining the products of an explosive decomposition.

(U) The above mechanistic interpretation of the decomposition of poly FA-BDE offers little hope for the desensitization of this material.

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SECTION VI

EXPERIMENTAL

A. PURIFICATION PROCEDURE (U)

1. INFO-635P (U)

(U)   The INFO-635P was received from Minnesota Mining and Manufacturing Company as a 10% solution in methanol, and was purified in the following manner. The methanol was evaporated by a stream of dry nitrogen. The dry solid was dissolved in nitromethane, in the proportion of 0.25 gram of INFO-635P to 1 cc. of nitromethane. To precipitate solid INFO-635P, ethanol-free chloroform was added in the proportion of 200 cc. chloroform to 1 cc. of nitromethane solution. The INFO-635P precipitated as a pale yellow, flaky solid. The solid was filtered and dried under a stream of dry nitrogen.

(U)   The dry INFO-635P was then washed with liberal amounts of diethyl ether which removed all traces of the yellow color. The solid was once more dried under a stream of dry nitrogen. After drying, the INFO-635P was powdered by brushing the solid lightly over a 60 mesh sieve. This gave a finely granulated, white powder. The melting point of INFO-635P, purified using this procedure, is in the range of 221° to 224°C.

2. BTU (U)

(U)   The BTU was received from American Cyanamid Company as a 5% dispersion in a halocarbon wax for safety in shipping and handling. To remove the wax and prepare the BTU for purification by sublimation, the procedure recommended by American Cyanamid was used. About 25 cc. of n-heptane were added to 4 g. of the wax dispersion and allowed to stand to dissolve most of the wax. The resulting slurry was transferred to a centrifuge tube, centrifuged, and the supernate decanted and discarded after treatment with aqueous potassium iodide solution. The BTU was washed with n-heptane three times, twice at room temperature and once at 60°C., then centrifuged. The residual heptane was removed from the impure BTU by pumping under reduced pressure. The impure BTU was purified by placing the impure material obtained from the wax dispersion into a sublimation unit containing a cold finger covered with a platinum foil sheath. The otherwise all-glass apparatus was made with a O-ring joint to avoid ground fittings. Sublimation was performed at 100°C., while the cold finger was kept at -60°C. to -50°C. via a flow of methylene chloride cooled with dry ice. Depending on specific conditions, the BTU sublimate formed either a tightly adherent layer or a loose crystal network around the cold finger.

3. Poly FA-BDE (U)

(U)   The poly FA-BDE used in this program was obtained from Esso Research and Engineering as a dilute solution in Freon 113. The polymer was separated in one gram quantities as needed according to the recovery instructions of J. A. Brown of Esso. The material was foamed by first evaporating most of the solvent with a stream of dry nitrogen and then suddenly exposing the resulting gummy solid to a good vacuum. Recovery in this manner produced a foamed material 5 to 10 times the volume of the original gummy solid. The fragile foam was then carefully broken up into small pieces and evacuated overnight to insure complete removal of the solvent.

B.   THERMAL DECOMPOSITION (U)

(U)   The slow thermal decompositions were performed in two all-monel systems, one of which is indicated schematically in Figure 27. For the experiments on INFO-635P, a 125 cc. monel Parr bomb was used as the reactor, whereas a 325 cc. bomb was used for the work on poly FA-BDE. Both reactors were equipped with a 0-30 psia. pressure transducer and a fast response thermocouple. Silicone oil baths were used for heating and both vacuum systems were connected directly to vapor phase chromatographs.

(U)   Samples of the oxidizers were weighed and placed in the reactor which was then attached to the vacuum line. After evacuation to less than 5 microns pressure, the valve on the reactor was closed to the vacuum line. Decomposition was started by raising the previously heated oil bath so that immersion of the reactor was complete up to the reactor shut-off valve. The pressure was recorded continuously and the temperature noted at intervals.

(U)   Decompositions were run under different conditions depending on the information desired. In early work where the overall progress of the decomposition was being studied, the product gases were allowed to accumulate above the decomposing solid and a continuous pressure-time curve recorded. The gases were sampled at intervals, chromatographed, and analyzed by mass and infrared spectroscopy. Data on the onset and early phases of decomposition were obtained by limiting the product gas pressure to only a few millimeters. In some instances, a continuous vacuum was maintained either cryogenically or mechanically. The gases were then trapped and removed for chromatography and analysis. For some work, a portable cycloidal mass spectrometer was connected to the exit of the chromatograph or directly to the reactor, for detection and identification purposes. Most of the chromatographic separations were performed using 20- and 25-foot columns packed with siloxane on Chromosorb W. The separation was usually performed at 0°C.

(U) For the work in which the decomposition of solid poly FA-BDE was followed, weighed samples were placed into Teflon cups contained by individual glass vessels and continuously evacuated during the experiment. The samples were removed at different time intervals and treated with Freon 113. The weight of the soluble portion, which gave an infrared pattern identical to the original poly FA-BDE, was taken as a measure of undecomposed poly FA-BDE.

C. MASS SPECTROMETRIC METHODS (U)

(U) The work using the method of mass spectroscopic thermal analysis (MTA) was done at the Eastern Laboratory of The Dow Chemical Company. A 1-2 mg. sample of material was pressed into one end of a tiny capillary 5 mm. long, which was then placed on top of a hollow monel probe 0.070 inch in diameter in the tip of which was a thermocouple. A miniature furnace was positioned around this unit, the final assembly being within about 2 mm. of the ionizing beam of a Bendix time-of-flight mass spectrometer. An ionizing voltage of 100 e.v. was used and the spectra recorded on a Visicorder at a chart speed of 25 inches per minute. The chamber of the mass spectrometer was initially at 10^{-7} Torr.

(U) The high resolution mass spectroscopy on INFO-635P and poly FA-BDE was done using a Consolidated 110 spectrometer. For this work, approximately 5 mg. samples were charged into one end of a passivated stainless steel capillary. The sample was then decomposed within a few millimeters of the ionizing beam by means of the heated probe of the mass spectrometer. Measurements of masses were made within 1 part in 20,000 for identification purposes.

D. SUPPLEMENTAL TECHNIQUES (U)

(U) The hot stage microscopy was performed with a Kofler micro hot stage in conjunction with an American Optical microscope. All observations were made at a magnification of 100X.

(U) Differential thermal analyses were run on a duPont 900 Differential Thermal Analyzer and the weight loss determinations made in a quartz spring thermobalance constructed at The Dow Chemical Company.

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SECTION VII

BIBLIOGRAPHY

1. JANAF Heat of Formation of Propellant Ingredients Table
    Dow Chemical Company, Series D, March, 1966.

2. Minnesota Mining and Manufacturing Company, "Chemical
    Research as Related to Advanced Solid Propellants," (U),
    Report No. 17, April 1 - June 30, 1963, Contract NOrd 18688.

3. Minnesota Mining and Manufacturing Company, "Chemical Research
    as Related to Advanced Solid Propellants," (U), Report No.
    1, January 1 - March 31, 1964, Contract NOw 64-0399-c.

4. The Dow Chemical Company, "Sensitivity Studies on NF Com-
    pounds," (U), AFRPL-TR-65-185, October, 1965, Contract
    Nr. AF 04(611)-9958.

5. U. S. Naval Ordnance Test Station, China Lake, California,
    "Research in Chemistry," (U), QPR July - September, 1965,
    NOTS Technical Publication 3940, Technical Progress Report
    418.

6. C.P.I.A., "Third Sensitivity Seminar on N-F Compounds," (U),
    June, 1965.

7. American Cyanamid Company, "Solid Rocket Propellant Research
    and Development," (U) Report No. 17, July 1 - September 30,
    1964, Contract NOrd 18728.

8. American Cyanamid Company, "Solid Rocket Propellant Research
    and Development," (U), Annual Report, 1965, Contract NOw
    65-0277-c.

9. The Dow Chemical Company, "Advanced Research on Solid Rocket
    Propellants," (U), Technical Summary Report AR-4Q-65,
    Contract Nr. AF 04(611)-7554(4).

10. American Cyanamid Company, "Solid Rocket Propellant Research
    and Development," (U) QPR No. 1, January 1 - March 31,
    1965, Contract NOw 65-0277-c.

11. Esso Research and Engineering Company, "Research on Advanced
    Solid Propellants," (U), QPR No. 63-4, September 1 -
    December 10, 1963, Contract DA-30-069-ORD-2487.

12. Esso Research and Engineering Company, "Desensitization of
    Available High-Energy NF Compounds," (U), Annual Report,
    July, 1965, Contract Nr. AF 04(611)-9969.

UNCLASSIFIED

13. Esso Research and Engineering Company, "Research on Advanced Solid Propellants," (U), QPR No. 64-1, December 11, 1965 - March 10, 1964, Contract DA-30-069-ORD-2487.

14. W. E. Garner, ed., "Chemistry of the Solid State," Butterworths Scientific Publications, London (1955).

15. The Faraday Society, "Molecular Mechanism of Rate Processes in Solids. A General Discussion of The Faraday Society," Aberdeen (1957).

16. F. P. Bowden and A. D. Yoffe, "Fast Reactions in Solids," Academic Press, Inc., New York (1958).

17. F. C. Tompkins, "Influence of Structure on Solid-State Reactions," Plenary Lecture Presented at the 5th International Symposium on the Reactivity of Solids, Butterworths, London (1965).

18. W. Feitknecht, Angew. Chem., Internat'l Edition, 4, 892 (1965).

19. R. Wollast, Industrie Chimique Belge, 30, 473-9 (1965).

20. W. Gomes, Nature, 192, 865-66 (1961).

21. P. W. M. Jacobs and F. C. Tompkins, "Classification and Theory of Solid Reactions," W. E. Garner, ed., "Chemistry of the Solid State," Butterworths Scientific Publications, London (1955).

22. C. E. H. Bawn, "The Decomposition of Organic Solids," W. E. Garner, ed., "Chemistry of the Solid State," Butterworths Scientific Publications, London (1955).

23. J. L. Mack and G. B. Wilmot, 3rd ICRPG Combustion Conference CPIA Publ. No. 118, September 1966.

24. P. W. M. Jacobs and A. R. T. Kareishy, "Kinetics of the Thermal Decomposition of Sodium Oxide," Proc. Roy. Soc., 4718 (1964).

25. The Dow Chemical Company, Quarterly Progress Report No. 3, 1 July - 30 September, 1966, Contract AF 04(611)-11395.

26. O. Knacke and I. N. Stranski, Progr. in Metal Phys., 6, 181 (1956).

27. J. P. Hirth and G. M. Pound, "Condensation and Evaporation Nucleation and Growth Processes," Pergamon Press, Oxford (1963).

28. C. F. Powell, J. H. Oxley, and J. M. Blocker Jr., Editors, "Vapor Deposition," John Wiley and Sons, New York.

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13. ABSTRACT The purpose of this research is to study the thermal decomposition of the solid oxidizers, INFO-635P, poly FA-BDE, and BTU. The objective is to obtain knowledge of their decomposition mechanisms and their relationship to the high sensitivity of these materials.

The degration of INFO-635P and poly FA-BDE was investigated chiefly by performing decompositions in the temperature range, 160°-180°C., under conditions of continuous vacuum, and low and high pressure of product gases. In addition, the technique of mass spectroscopic thermal analysis (MTA), complemented by high-resolution mass spectroscopy, was used to study the decomposition under high vacuum where secondary reactions were minimized.

Examination and interpretation of the experimental data have shown that INFO-635P may decompose, after nucleation, by one or more of several paths simultaneously. This multiplicity of reaction mechanisms is mainly a result of the sublimation of INFO-635P, which appears to obey a first order rate law. This physical process is presumed to occur after a series of reactions in the solid phase involving proton transfer and desorption from the solid. Suggestions for desensitization of INFO-635P are given.

The early gaseous products of the poly FA-BDE decomposition were identified, and related to the solid phase reaction. The residue was an insensitive and insoluble material believed to be a highly crosslinked polymer. Mechanisms are proposed for the early degradative steps which explain the formation of the observed products. The experimental results give little hope for the desensitization of this material.

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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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INFO-635P, Decomposition of						
FA-BDE, Poly						
FA-BDE, Poly, Decomposition of						
BTU						
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